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Final Report

for

Sealing of Silver Oxide-Zinc Storage Cells

N69-12309

Contract No.: NAS 5-10409

Prepared by:

Astropower Laboratory
Missile & Space Systems Division
Douglas Aircraft Company
McDonnell Douglas Corporation
Newport Beach, California

for

Goddard Space Flight Center
Greenbelt, Maryland

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ABSTRACT

Use of miniature fuel cells in controlling pressure in sealed silver oxide-zinc storage cells is described here. These fuel cells are miniature electrochemical devices composed of one solid battery electrode and one fuel cell gas consuming electrode. They are installed on or in a silver oxide-zinc storage cell and perform their pressure control function by electrochemically consuming evolved gases (H_2 and O_2) from the storage cells.

The initial phase of this work concerned measuring the gassing characteristics of a group of commercial 16-Ah silver oxide-zinc storage cells under four different operating modes. The second phase consisted of designing and fabricating miniature fuel cells to accommodate these gassing rates. The third phase involved assembly and test of composite storage cell-miniature fuel cell assemblies in the sealed condition under the same operating modes as above. The fourth and final phase involved fabrication and delivery of fifteen composite assemblies to NASA Goddard.

The most significant results were obtained in the third test phase. Here it was demonstrated that a group of series connected assemblies could be operated for extended periods in the sealed condition without excessive pressure rise. In one test a group of eight sealed assemblies was operated on a continuous 24-hour cycle regime for nearly 4000 hours. Effective operation in the sealed condition was also demonstrated for a group of eight fully charged assemblies on stand at both room temperature and at 0°C for over 3000 hours. Some problems were encountered in initial attempts to operate eight such assemblies on a continuous 90-minute cycle regime. These difficulties were found to be associated with the initial method of regenerating the fuel cells. The problems were resolved by modifying the regeneration processes.

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SUMMARY AND CONCLUSIONS

The purpose of this program was to evaluate the use of miniature hybrid fuel cells in controlling pressure in sealed silver oxide-zinc storage cells. The fuel cells perform this function by electrochemically consuming evolved hydrogen and oxygen. Two different fuel cells were used for this purpose. The first consisted of a silver oxide cathode in conjunction with a hydrogen-consuming anode. The second consisted of a cadmium anode in conjunction with an oxygen-consuming cathode. These fuel cells and systems including such fuel cells for controlling pressure in and sealing batteries, including silver-zinc batteries, are proprietary with McDonnell Douglas Corporation, and are covered in one or more pending patent applications of McDonnell Douglas Corporation. The silver oxide-zinc storage cells employed in this program were commercially available 16-Ah high rate units.

The program was designed to achieve the following specific objectives.

1. Establish the general gassing characteristics of the silver-zinc cells intended to be mated with the micro fuel cells. Commercially available, secondary silver-zinc cells of approximately 16 ampere-hours capacity should be tested under the following regimes:

   a. 24-hour orbit at 25°C: 23-hour charge to a 1.98 volt/cell cutoff and maximum current of 500 ma and 1-hour discharge at a 5-ampere rate (amended 9/7/67).

   b. 90-minute orbit at 25°C: 1-hour charge to a 2.05 volt/cell cutoff and maximum current of 3.0 amp and 30-minute discharge at a 5-ampere rate (amended 9/7/67).

   c. Open circuit stands at both 0°C and 25°C.

2. Optimize the performance and design of a micro fuel cell system to accommodate these gassing characteristics, to be mountable on or within a storage cell, and to be rechargeable by electrochemical interaction with the storage cell and its charging circuit. Hydrogen-silver oxide and cadmium-oxygen fuel cell couples appear to be the most promising. Determine whether or not a single micro fuel cell will be sufficient for consuming both hydrogen and oxygen.

3. Assemble and test for 250 cycles, or until failure, 24 composite units consisting of high rate, sealed, silver-zinc storage cells with incorporated micro fuel cells of the optimized design determined above from (2). The same test regimes as outlined in (1) above should be employed.

4. Monitor and record the performance of the storage cells and the fuel cells during the testing of these units, to include the following parameters: temperature, voltages, currents, cell pressures, storage cell cycling efficiency and capacity retention, fuel cell recharge frequency and efficiency.

5. Evaluate the capability of sealing silver-zinc cells in this manner for use in a practical, spacecraft-type, power supply system, by comparing the test results of (3) and (4) above with the design performance and reliability requirements for such a power supply.

Results have demonstrated that the micro fuel cells are quite effective in sealing AgO-Zn storage cells. With proper design and installation in the AgO-Zn cells, they form composite sealed assemblies capable of operating over a range of conditions without excessive pressure rise. The feasibility of employing the micro fuel cells in practical space power systems appears favorable in that they perform their function without impairing the performance of the AgO-Zn cells, without excessive power drain, with little or no maintenance requirements, and with only a small weight penalty of less than 12% of the weight of the AgO-Zn cells. Since these AgO-Zn cells had not been designed to accommodate the micro fuel cells, it is expected that this figure would be significantly lower for a more appropriately designed AgO-Zn cell.

The most significant results of the program are tabulated below.

GASSING STUDIES UNDER PHASE I

1. Very low to moderate gassing rates were noted for eight series connected cells on the 24-hour regime. Maximum average rates in a given cell for O_2 were 0.11 cc/hour and for H_2 1.4×10^{-3} cc/hour for a period of 1944 hours.

2. Moderate to high gassing rates were noted for eight series connected cells on the 90-minute regime. Maximum average rates in a given cell were 3.5 cc/hour for O_2 and 1.1 cc/hour for H_2 for a period of 624 hours.

3. No measurable quantities of gas were evolved from any of four cells on stand at 0°C in the fully charged state for 1944 hours.

4. Very low H_2 rates (approximately 1 cc/day) were evolved from two cells during the first few weeks of stand at room temperature in the fully charged state. Thereafter, these cells did not evolve any measurable quantities of gases through the end of the test after 1944 hours. Two other cells did not evolve any gases throughout this period under the same condition.

MICRO FUEL CELL STUDIES UNDER PHASE II

1. Cadmium type micro fuel cells can be discharged effectively at current densities to 100 mA/cm^2. For the 1.0 cm^2 cells employed here, this signifies O_2 consumption rates to 21 cc/hour. Efficiencies

based on weight of Cd vary from 27 to 50%, depending on thickness of the Cd electrode and operating current densities.

2. Silver oxide micro fuel cells can be discharged effectively at current densities to 100 mA/cm^2. For the 1.0 cm^2 cells employed here, this signifies H_2 consumption rates to 42 cc/hour. Efficiencies based on weight of AgO vary from 43 to 74%, depending on thickness of the AgO electrode.

SEALED CELL TESTS UNDER PHASE III

1. Eight composite assemblies were successfully operated in series for 158 cycles or 3792 hours on the 24-hour cycle regime. The AgO micro fuel cells were operated in the primary mode throughout and the Cd micro fuel cells were operated in both the primary and secondary mode with separate charge circuits. Maximum pressure developed in any given assembly was only 0.84 Kg/cm^2 gage (12 psig). Estimated pressure based on integrated micro fuel cell currents would have been 137.5 Kg/cm^2 gage (1956 psig) without micro fuel cells. Cycling efficiencies of the AgO-Zn cells were at least 95% and residual capacities of at least 3 cells were at least 19 Ah at the end of the test. Surface temperatures of the AgO-Zn cells were never more than 1^o above room temperature.

2. Eight composite assemblies were initially operated in series on the 90-minute cycle regime. The AgO micro fuel cells were operated in the primary mode and the Cd micro fuel cells were operated in the secondary mode with a parallel charge circuit. Five of these assemblies exhibited premature failures during the early stages and were removed from test. These failures were not attributed to the fuel cells per se, but to the method of charging them. An individual charge method was subsequently adopted which permitted successful completion of the test with the remaining three assemblies. These three assemblies completed 606 cycles or 909 hours on this regime in the sealed condition. Maximum pressure developed in any given assembly was 1.27 Kg/cm^2 gage (18 psig). Estimated pressure based on integrated micro fuel cell currents would have been 159.1 Kg/cm^2 gage (2269 psig) without micro fuel cells.

3. Four composite assemblies successfully completed a stand test in the fully charged state for 3264 hours at room temperature. Extremely low gassing rates were noted from micro fuel cell currents in all assemblies and pressures in all were no greater than atmospheric throughout. Maximum H_2 and O_2 rates were 0.2 cc/day and 0.005 cc/day, respectively. Capacity retention of each of the four silver-zinc cells was near 19 Ah or 85% of original formation capacity for the complete period. An explanation for the observed low gassing rates is given herein.

4. Four composite assemblies successfully completed a stand test in the fully charged state for 3288 hours at 0°C. Extremely low gassing rates were again noted in each of the assemblies from the micro fuel cell currents; internal pressures in each were never greater than atmospheric throughout. Maximum H_2 and O_2 rates were 0.2 cc/day and 0.01 cc/day respectively. Capacity retention of all four silver-zinc cells was near 8 Ah or 50% of rated capacity for the complete period. An explanation for the observed low gassing rate is given herein.

5. The micro fuel cells can be effectively recharged in situ without evolution of gases and with little or no maintenance requirements. This can be done with either an auxiliary power supply or by the host AgO-Zn cell without any significant degradation in performance of the AgO-Zn cell. The AgO micro fuel cells seldom need recharge because of the low H_2 rates on most regimes. In some cases, these cells could be operated in the primary mode for the entire duration of the mission. The Cd micro fuel cells do require frequent or even continuous recharge because of the high O_2 rates found on most regimes. Maximum required continuous currents for the Cd cells range from approximately 5 to 50 mA, depending on the charge rates and cutoff voltages of the AgO-Zn cells.

FABRICATION OF SEALED UNITS UNDER PHASE IV

Fifteen sealed composite assemblies were fabricated and delivered to NASA Goddard for evaluation. Each of these consists of a 16 Ah AgO-Zn cell with incorporated dual micro fuel cell assembly (AgO and Cd). Figure 1 is a photograph of these units.

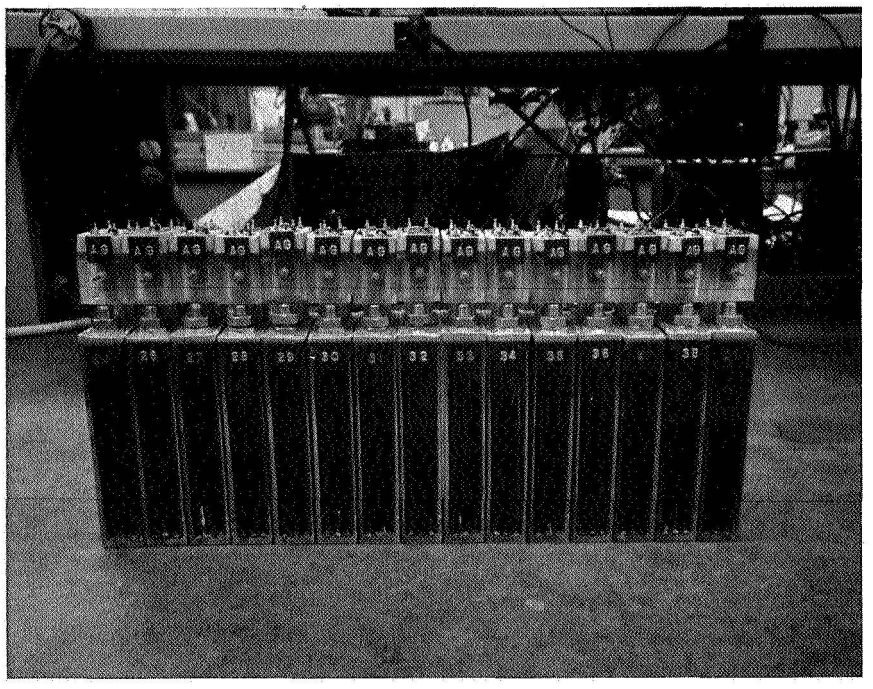

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Figure 1. Photograph of 15 Composite Assemblies Delivered to NASA/Goddard

INTRODUCTION

The objective of this program is to evaluate the capability of hybrid micro fuel cells in controlling pressure rise in silver oxide-zinc cells and thereby permitting operation of these cells in the hermetically sealed condition. The micro fuel cells perform this function by electrochemically consuming evolved battery gases consisting of hydrogen and oxygen.

This program is a continuation of work performed previously by Astropower Laboratory for the NASA/Goddard Space Flight Center (Reference 1). The approach employed on the preceding program involved the use of "true" rather than "hybrid" fuel cells.

The micro fuel cells on the present program contain one gas and one solid electrode instead of two gas electrodes; as such, they may be considered hybrid storage/fuel cells. Two types are again involved, one for consuming hydrogen and the other for consuming oxygen. The hydrogen-consuming fuel cell consists of a solid metal oxide cathode (AgO) and a platinum hydrogen anode. The oxygen-consuming cell consists of a solid metal anode (Cd) and a platinum oxygen cathode. These couples were selected on the basis of their known stability, recharge capability and capacity (Reference 2). These fuel cells are installed in the storage cell head space or in an adapter connected to this head space and perform their function by electrochemically consuming evolved gases in accordance with the following overall reactions.

$$\text{Consumption of } H_2\text{: } AgO + H_2 \rightarrow Ag + H_2O \quad (1)$$

$$\text{Consumption of } O_2\text{: } 2Cd + O_2 + 2H_2O \rightarrow 2\,Cd(OH)_2 \quad (2)$$

These new hybrid micro fuel cells offer several advantages over the original H_2-O_2 types and should be more widely applicable to sealing batteries in future space missions. First, they require no O_2 or H_2 storage because their oxidant and fuel supply are contained within their solid electrodes. Second, they require no gas manifold system to distribute gases from storage tanks to the individual cells. Third, they require no pressure control devices to regulate supply pressure within specified limits. The new hybrid micro fuel cells are self-contained units and may be installed directly into and form an integral part of the silver oxide-zinc cell.

The amount of gases that the hybrid fuel cells can consume depends on the amount of solid battery electrode (AgO and Cd) and the discharge efficiency. Nominal capacities of the fuel cells used here were 2 Ah for both the AgO and Cd types. When the fuel cells have been discharged they can be subsequently recharged to regain essentially 100% of their rated capacity. This process is carried out in situ without evolution of gases by charging the solid fuel cell electrodes against the AgO-Zn electrodes using incorporated wicks as electrolyte bridges. The Cd micro fuel cell electrode is charged against the Zn anode of the AgO-Zn cell while the AgO micro fuel cell electrode is charged against the AgO cathode of the AgO-Zn cell. The following reactions take place:

Charge of Cd Fuel Cell

Anode of Cd fuel cell:	$Cd^{++} + 2e^{-} \rightarrow Cd$	(3)
Anode of AgO-Zn cell:	$Zn \rightarrow Zn^{++} + 2e^{-}$	(4)
Overall:	$Cd^{++} + Zn \rightarrow Zn^{++} + Cd$	(5)

Charge of AgO Fuel Cell

Cathode of AgO fuel cell:	$Ag + 2(OH)^{-} \rightarrow AgO + H_2O + 2e^{-}$	(6)
Cathode of AgO-Zn cell:	$AgO + H_2O + 2e^{-} \rightarrow Ag + 2(OH)^{-}$	(7)
Overall:	$\underset{(FC)}{Ag} + \underset{(Bat)}{AgO} \rightarrow \underset{(Bat)}{Ag} + \underset{(FC)}{AgO}$	(8)

This method of operating the fuel cells permits use of small units with extensive gas consumption capabilities.

The experimental program was divided into four phases some of which were carried out simultaneously. These included the following:

Phase I: Determine the gassing characteristics of the silver-zinc cells under four different operating regimes;

Phase II: Design and test micro fuel cells to accommodate the gassing rates in these cells;

Phase III: Evaluate composite micro fuel cell/silver-zinc cells in the sealed condition under the same regimes as indicated above;

Phase IV: Assemble and deliver 15 sealed silver oxide-zinc cell/micro fuel cell composites to NASA/Goddard for evaluation.

The feasibility of sealing AgO-Zn cells with micro fuel cells for use in a practical, spacecraft power supply system was to be determined from the results of the above phases.

TECHNICAL DISCUSSION

EXPERIMENTAL DETAILS

This section contains a complete description of the micro fuel cells and AgO-Zn cells and details of tests performed on them.

Description of AgO-Zn Cells

Altogether, a total of 63 AgO-Zn cells were used on this program. Twenty-four of these were used in the gassing studies of Phase 1; 24 others were used in the sealed cell tests of Phase III; and the final 15 were incorporated in the sealed assemblies that were delivered to NASA/Goddard.

All of the cells were identical and were classified as 16 Ah high rate, silver oxide-zinc cells. Actual capacity of each was near 22 Ah. Overall dimensions of each cell were 5.7 cm x 12.2 cm x 2.0 cm (including terminals). Dry weight of each was 218 grams, and wet weight (after activation) was 285 grams. The cells were purchased from a leading manufacturer of silver oxide-zinc cells.

The cells were received from the manufacturer dry and unformed. To prepare them for test, it was necessary to carry out two preliminary steps including activation and formation. These procedures were carried out in accordance with the manufacturer's recommendations with the exceptions noted below.

Activation was carried out by filling each cell with 48 cc of supplied electrolyte. To avoid overflow, it was necessary to carry out this addition with application of a vacuum of 635 to 750 mmHg. The cells were then left on stand for 72 hours to complete the activation step.

At this point, the cells were arranged in series in groups of 8 to 12, depending upon the number to be processed at a given time. Formation charge was then carried out on each group at a current on 0.7 amperes until the voltage of all cells within the group was at least 2.05 volts. The group of cells was then carried through formation discharge at a current of 5.0 amperes until the voltage of the first cell reached 1.0 volt. These formation cycles were carried out in the vented condition at least three times in accordance with the manufacturer's recommendations. Three additional cycles were carried out on the 24 cells of Phase III and the 15 cells delivered to NASA/Goddard. The purpose was to rid the cells of oxygen which was noted to be evolved during the early stages of cycling in Phase I. It was believed that this would avoid placing an extra and unnecessary burden on the Cd micro fuel cells during the early stages of tests in the sealed condition.

Description of Micro Fuel Cells

The micro fuel cells used in this program were small, cylindrical units with 1.5 cm O.D.and overall lengths ranging from 1.0 to 3.0 cm. Components of some of the earlier models used in the design studies of Phase II are shown in Figures 2 and 3, and components of the later units delivered to NASA/ Goddard are shown in Figure 4.

The AgO micro fuel cells are composed of a silver oxide cathode, a fuel cell type H_2 anode, an inorganic separator, and KOH electrolyte. The silver oxide cathode is prepared by pressing and thin sintering commercially available silver powder into the form of a pellet. A silver wire is embedded in the electrode and extends from it for external contact. The electrode is then formed in a KOH bath to produce the AgO electrode. The H_2 anode of this cell is made from a commercially available fuel cell electrode (American Cyanamid Type AB-40). The electrode is prepared by cutting a disc from this material with a suitable diameter punch and spot welding a gold wire to the electrode for external electrical contact. Separator material is a proprietary inorganic type in the form of a thin disc. Wick material is nylon felt. This is cut from roll stock as shown in Figure 4. Cases for the micro fuel cells are machined from lucite stock.

The Cd micro fuel cells are quite similar to the AgO cells in that they both have the same overall dimensions and case design and both employ the same type of fuel cell electrode and electrolyte. The only major differences are in the Cd anode and separator. The Cd anode is made from the same type of Cd powder that is used in the anodes of commerical Ni-Cd cells. The powder is pressed into a pellet in a die. Two thin silver wires are embedded in the electrode and extend from it for external electrical contact. The separator for this cell is commercially available fuel cell grade asbestos from Johns Manville. This is cut from sheet stock with a punch. The oxygen cathode of this cell is identical to the H_2 anode of the AgO cell. A gold wire is again spot welded to this cathode for external electrical contact.

Measurement of Gassing Under Phase I

Gassing rates of the AgO-Zn cells under Phase I were determined by water displacement. Small diameter (0.1 cm I.D.) tubing was used to transmit the gases from each AgO-Zn cell to an inverted cylinder filled with water (see Figure 5). Gassing rates were calculated from observed changes in volume with time. When a sufficient volume of at least a few cc's had been collected, the graduate was removed and a small sample (50 $\mu\ell$) was taken for chromatographic analysis. This analysis was performed on a Beckman Model G. C. 2A gas chromatograph. After the analysis was completed the graduate was refilled with water and inverted for collecting more gases. These measurements were performed regularly on each of the 24 cells in Phase I cycle and stand tests.

Testing Micro Fuel Cells Under Phase II

Performance characteristics of the micro fuel cells under Phase II were determined under simulated battery gassing environments. These environments

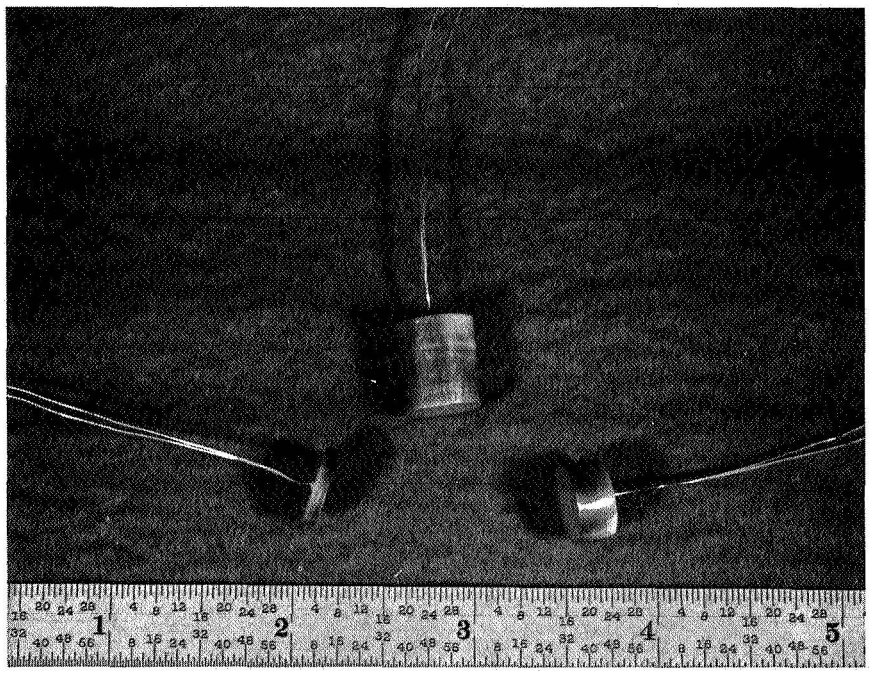

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Figure 2. Electrodes for AgO and Cd Micro Fuel Cells

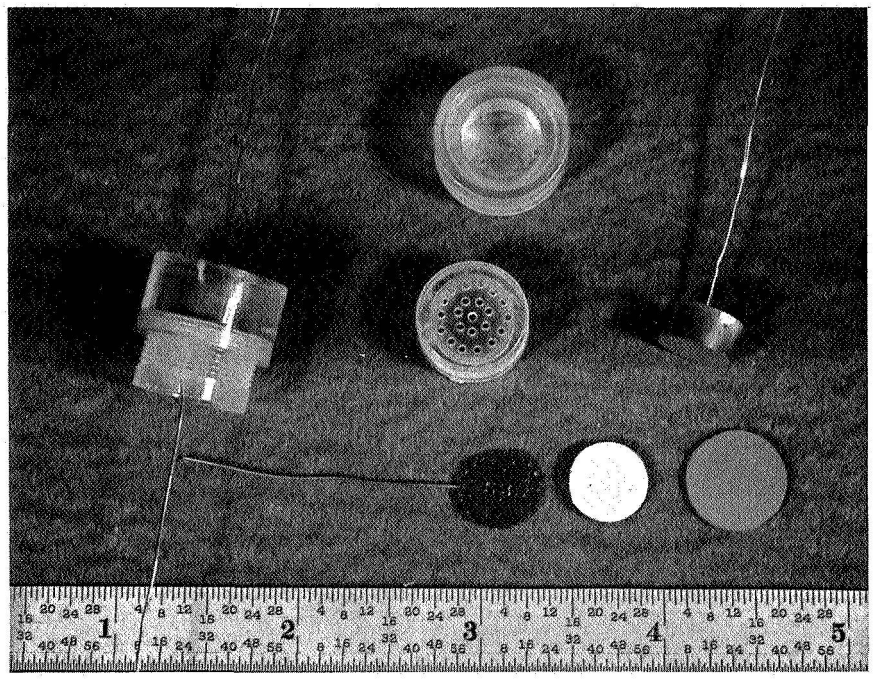

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Figure 3. Components of AgO and Cd Micro Fuel Cells

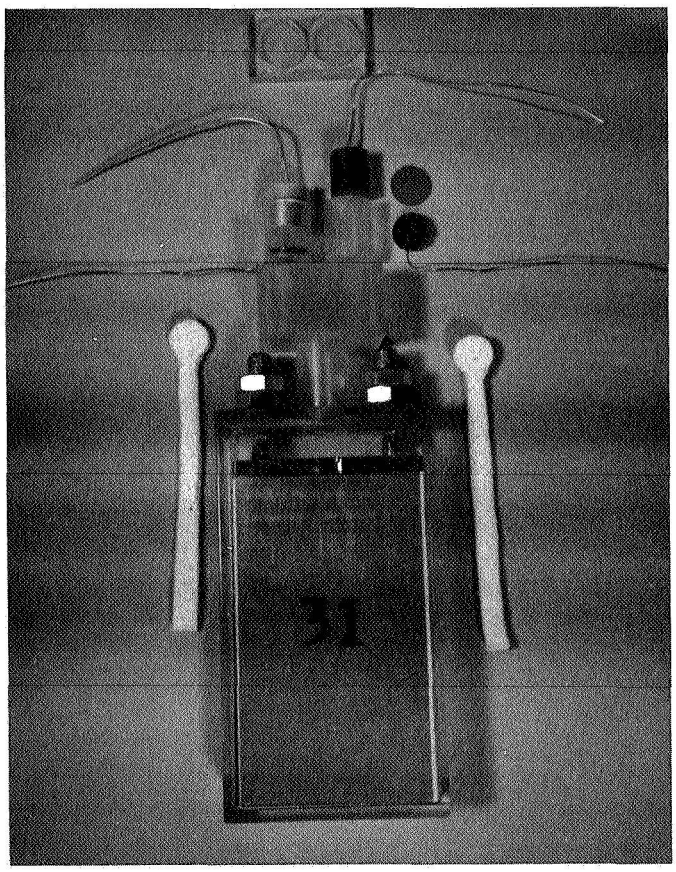

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Figure 4. Composite Micro Fuel Cell-Silver Zinc Cell Assembly

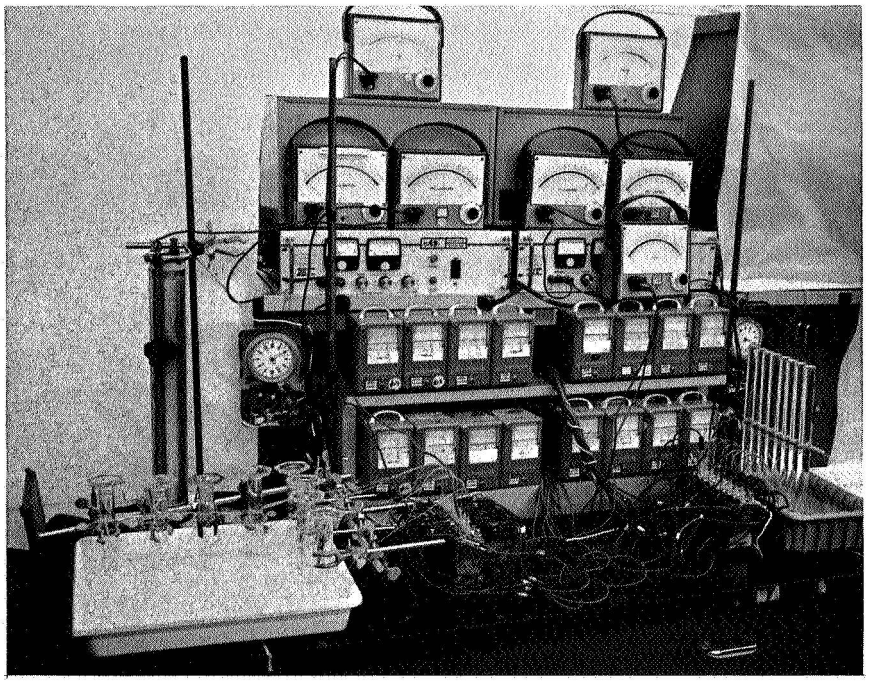

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Figure 5. Measurement of Gassing in Silver Oxide-Zinc Cells Via Water Displacement

corresponded to the gas head space of AgO-Zn cells and consisted of small containers filled partially with KOH solution and flushed slowly with H_2 or O_2 gases, depending upon the type of micro fuel cell under test. The fuel cell was suspended above the KOH solution and was in contact with it via a nylon felt wick. Electrical leads of the micro fuel cell were passed through the cover of the container for external contact.

The micro fuel cells were cycled at constant current for both charge and discharge. For short term (overnight) runs at high rates, the cell voltages were recorded continuously with miniature Rustrak voltmeter recorders. For long term runs at low rates, lasting for several days or even weeks, the cell voltages were recorded manually a few times each day. Cell polarization data were also determined periodically during the course of a cycle. Constant current operation was interrupted for only a few minutes for these measurements. Gas consumption rates were calculated from operating currents. Total gas consumption capability was determined by integrating current-time curves and converting to equivalent volume of gas.

Description and Operation of Composite Assemblies

Figure 6 is a detailed drawing of the composite assemblies used in Phase III and Figure 7 is a photograph of these units. The 15 units delivered to NASA/Goddard are identical to these except for minor changes in the outside dimensions of the adapters for the micro fuel cells.

Each composite assembly consists of a commercial 16 Ah, AgO-Zn cell equipped with a dual micro fuel cell assembly. The micro fuel cells are installed inside a rectangular adapter which in turn is installed on the top case of the AgO-Zn cell. The micro fuel cells are suspended from the top cover of the adapter with their gas consuming electrodes on the bottom facing the vent port of the AgO-Zn cell. The micro fuel cells are held in place by cementing the ends of their Lucite cases to the inside top cover of the adapter with a small amount of ethylene dichloride. Each micro fuel cell is equipped with a wick that extends from the top of its solid electrode through the adapter and into the electrolyte of the AgO-Zn cell. Electrical leads from the micro fuel cells are passed through the top cover of the adapters for external electrical contact. These wires are connected to binding posts which are cemented to the top of the adapter with epoxy. Total weight of the fuel cell assembly is 35 grams.

No special precautions were necessary for operating the AgO-Zn cells. They were set up for test in a conventional manner (see next sections) and operated as any other battery.

Aside from an occasional recharge, there were no special maintenance requirements involved in operating the micro fuel cells. They were placed in operation by merely providing an external electrical contact between their anodes and cathodes. This activated them for consuming internal gases. Thereafter, the micro fuel cells performed their function automatically.

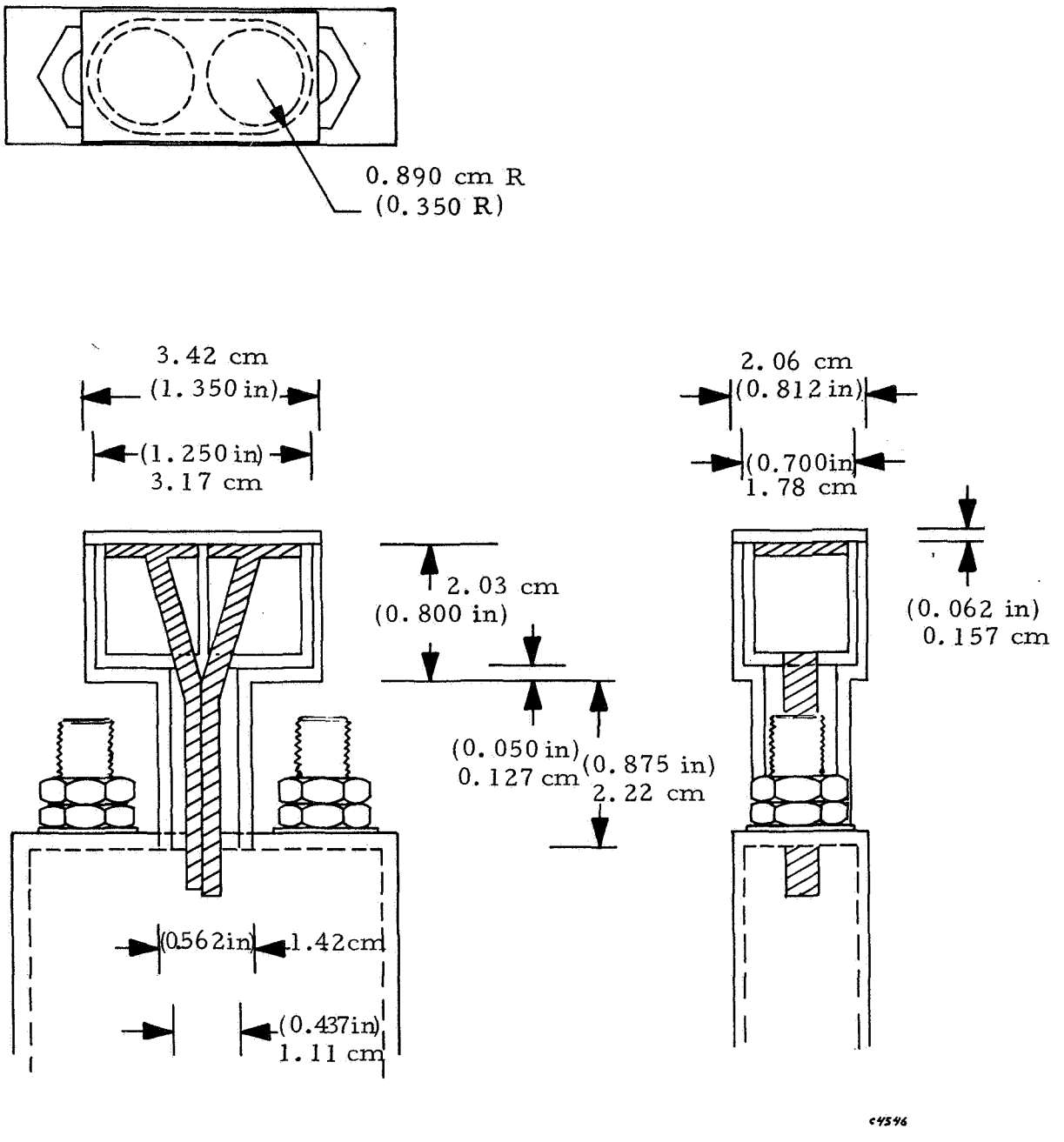

Figure 6. Dimensions of Composite Assembly

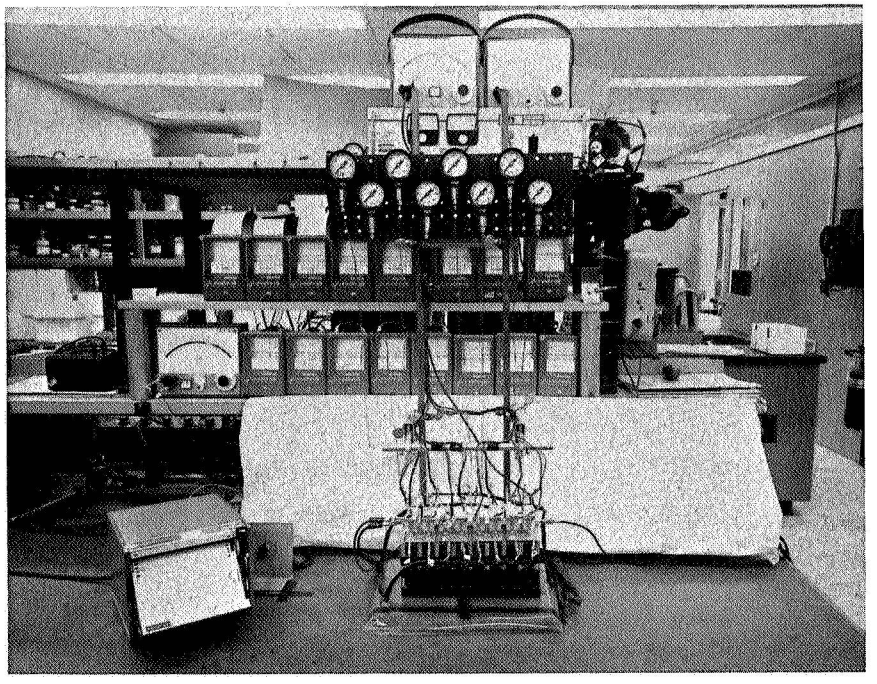

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Figure 7. Eight Composite Assemblies on 24-Hour Cycle Test

Two methods of charging the Cd micro fuel cells were attempted on this program. One of these methods proved successful while the other was found to cause degradation of the AgO-Zn cells. Figure 11 is a schematic diagram of the successful method and is discussed below. The method involved use of a separate power supply for each micro fuel cell. Charge was applied on an individual basis only to those Cd cells that had become discharged. This state was determined by comparing integrated current-time output with known initial capacity. The state of complete discharge was also confirmed when it was noted that a Cd cell did not respond to a positive O_2 pressure. Electrical connections were arranged so as to avoid generation of oxygen at the fuel cell cathode. This was carried out by connecting the negative terminal of the power supply to the Cd micro fuel cell electrode and the positive terminal of the supply to the Zn electrode of the AgO-Zn cell. Current was held constant at 10 mA (10 mA/cm^2) until the Cd electrode was fully charged and began to evolve hydrogen. This point was determined by a sharp rise in output of the AgO micro fuel cell which senses the evolved hydrogen.

The second method of charging the Cd micro fuel cells involved use of a single power supply and a parallel charge network. Details of this method and modifications are described later.

Throughout the course of this program, there was no need to recharge any of the AgO micro fuel cells. In the event that this would have been required, it could have been carried out in an analogous manner to that used in charging the Cd cells. Electrical connections are arranged so as to avoid hydrogen evolution at the fuel cell anode. This could be done by connecting the positive terminal of the supply to the AgO micro fuel cell electrode and the negative terminal of the supply to the AgO electrode of the AgO-Zn cell. Charge is again carried out at constant current of 10 mA until the AgO micro fuel cell is completely charged and begins to evolve oxygen. This point is signalled by a sharp rise in output of the Cd micro fuel cell which senses the evolved oxygen.

Details of 24 Hour Cycle Test Under Phase I

Eight AgO-Zn cells were operated in series on this 24-hour cycle test. Charge was carried out under a modified constant current method with a regulated dc power supply (Sorenson Model DCR 40-10A). Charge time was 23 hours with an upper current limit of 500 mA and cutoff voltage of 1.98 volts/cell. For eight cells in series, this upper cutoff was therefore 8 x 1.98, or 15.84 volts. The power supply was set slightly higher than this value to compensate for IR drop in the lines. Discharge was carried out across a fixed resistive load which was selected to give an average current of 5 amperes for the 1-hour discharge period. The test was interrupted for a short term after 1320 hours for special trickle charge and capacity determination.

Voltages of each of the AgO-Zn cells were recorded continuously with miniature Rustrak voltmeter recorders. Charge current was measured periodically by connecting a recorder across a shunt in the series line. Discharge current was recorded manually during the 1-hour discharge period each day. Gassing rates and gas composition were determined by water displacement and gas chromatography as described earlier. The cells were

arranged in series and numbered 9 through 16 inclusive with #9 located at the positive end of the stack.

Details of 24-Hour Cycle Tests Under Phase III

Eight AgO-Zn cells were operated in series in this 24-hour cycle test of Phase III. Cycle conditions for these cells were identical to those used on the 8 cells of Phase I. Voltage and current of the AgO-Zn cells were also recorded in the same manner as above. The micro fuel cells were installed in an adapter and mounted on the AgO-Zn cells as shown in Figure 6.

The AgO micro fuel cells were operated in the primary mode throughout the entire test. Current output of these micro fuel cells were found to be relatively constant; the values were recorded once each day.

All of the Cd micro fuel cells were operated in the primary mode for the first 600 hours or 25 cycles. Thereafter, some of the Cd cells were operated in the secondary mode. These were charged separately as required with auxiliary power supplies in the manner described above. Output currents of the Cd cells were recorded continuously with miniature Rustrak milliammeter recorders. Internal pressures of the AgO-Zn cells were recorded at least once each day from installed pressure gages.

The assemblies were arranged in series and numbered 11 through 18 inclusive with #11 located at the positive end of the stack.

Details of 90-Minute Cycle Tests Under Phase I

Eight AgO-Zn cells were operated in series on this 90-minute cycle test under Phase I. Charge and discharge times were 60 and 30 minutes, respectively. Charge was carried out under modified constant current method with a regulated dc power supply (Sorenson Model DCR 40-10A). It was originally planned that a charge current limit of 3.0 amperes and an upper cutoff voltage of 2.05 volts/cell be used. Discharge was to be carried out across a fixed load selected to give an average current of 5.0 amperes for the 1/2-hour discharge period. During the last 624 hours, these conditions were maintained. During the first 1320 hours, however, there was a small discrepancy in the upper cutoff voltage. The actual cutoff during this period was 2.02 volts/cell or 16.16 volts overall as compared with the desired value of 2.05 volts/cell or 16.40 volts overall. This discrepancy was due in part to a faulty voltmeter and in part to neglect of a small IR drop in the lines. As will subsequently be pointed out, this small error had a marked effect on gassing rates. These gassing rates and gas compositions were determined in the same manner described earlier. This test was interrupted for a short time after 1320 hours to carry out special trickle charge and capacity tests. The cells were arranged in series and were numbered 17 through 24 inclusive with #17 at the positive end of the stack.

Details of 90-Minute Cycle Tests Under Phase III

It was originally planned that this test be carried out with eight AgO-Zn cells in a similar manner to the above. These were to be operated on the 90-minute regime with 2.05 volt/cell cutoff and 3.0 amperes charge limit and 5.0 amperes discharge. The AgO micro fuel cells were to be operated in the primary mode and the Cd micro fuel cells were to be operated in the secondary mode. The eight Cd cells were to be given continuous trickle charge in a parallel arrangement. This was to be carried out under a modified constant current method with an upper voltage cutoff corresponding to the state of full charge of a Cd micro fuel cell. This method would provide for distribution of current in proportion to the state of charge of the micro fuel cells and tapering of current when all cells were fully charged. This, in turn, would prevent overcharge and subsequent evolution of hydrogen. Initial current was to be set at a value corresponding to the maximum oxygen evolution rate.

The assemblies were arranged in series and numbered 1 through 8 inclusive with #1 at the positive end of the stack.

Several unsuccessful attempts were made to run the test in the manner just described. Each of these differed slightly from one another in the details of the parallel charge circuit. The first run was carried out with eight sealed assemblies set up in accordance with the circuit diagram of Figure 8. Cycle conditions for the AgO-Zn cells were the same as described above. Operating voltages and internal pressures were recorded continuously with miniature Rustrak recorders. The AgO micro fuel cells were operated in the primary mode via discharge across 10.0 ohm precision resistors. Currents of the AgO micro fuel cells were determined periodically by measuring the voltage drop across these resistors. The Cd micro fuel cells were operated in the secondary mode from the start. Charge was carried out with a regulated auxiliary power supply as shown in Figure 8. The positive terminal of this supply was connected via a parallel network to each of the negative (zinc) terminals of the AgO-Zn cells. The negative terminal of the supply was connected via another parallel network to the negative (Cd) electrodes of each micro fuel cell. Each branch of the negative parallel network contained a protective diode (Motorola 1N4001). These diodes were to prevent shorting of the AgO-Zn cells through the micro fuel cell circuits. Overall current was set at 160 mA to correspond to a current of 20 mA for each of the eight Cd electrodes. Current distribution in each of the branches was determined periodically by installing a milliammeter in each of the lines. These measurements were made on both the negative and positive branches of the Cd charge circuit.

In addition to being charged in the above manner, the Cd micro fuel cells were also on simultaneous discharge. Each of the cells was on essentially a direct short through miniature Rustrak milliameter recorders. These recorders gave a continuous record of micro fuel cell output and corresponding oxygen consumption rate.

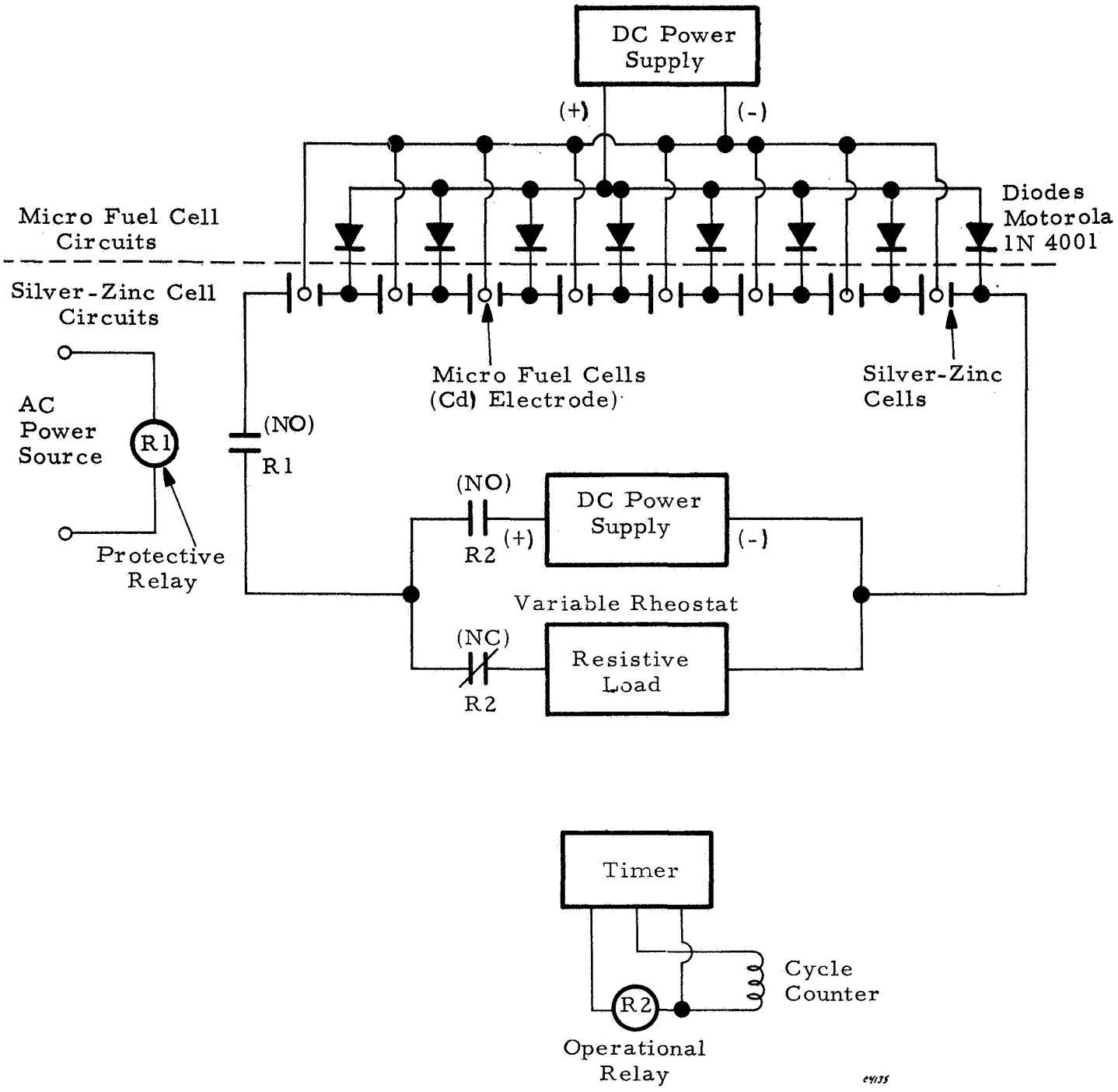


Figure 8. Original Circuit for Silver-Zinc Cells and Cd Micro Fuel Cells on 90 Minute Cycle Regime

Operation in the above mode was terminated after 48 hours for reasons described under Results, below. The circuit was modified at this point by installing protective diodes in the intercell connections (IRC Silicon Power Rectifiers Part No. 20HB20-C). These particular diodes were selected on the basis of their availability and usefulness for the application. It was realized that improved diodes could be obtained later if the concept was found to be worthwhile. These diodes were installed in the intercell connections in conjunction with a set of relays (see Figure 9). These relays opened the diode branch of the intercell contacts for charge and closed the branch for discharge. This directed the discharge current through the diodes and the charge current directly across the relay contacts. The charge circuits to the Cd micro fuel cell electrodes were also equipped with a set of relays which placed them on charge only while the silver-zinc cells were on discharge. When the silver-zinc cells were on charge, the relays opened each of the negative branches of the parallel Cd charge circuit. All of these relays were operated by the same timer that controlled the Ag-Zn cells. This arrangement avoided intercell leakage currents. All other details of operation in this phase were identical to the original phase described above with one exception. This was an adjustment of external load to maintain the required 5.0 amps discharge current. Lower currents would have been obtained without this adjustment, due to the lower overall voltage resulting from the diodes. The assembly was run for 50 hours in this manner.

At this point, the circuit was modified again by replacing the intercell diodes with power transistors (Motorola Type 2N2158). The purpose of this change was to reduce the voltage losses and thereby improve overall voltage and power output of the Ag-Zn cells. Figure 10 is a schematic diagram of the circuit with these transistors. A set of relays was used again to open the transistor branch of the intercell connections for charging the Ag-Zn cells and to close this branch for discharge. This directed the discharge current through the transistors and the charge current through the relay contacts. Two additional sets of relays were also required here. One was used to apply (-12) volts to the bases of the transistors to turn them on for discharge, and another was used to apply (+16) volts to the bases of the transistors to turn them off during charge. Another set of relays provided for charging the Cd micro fuel cell electrodes only while the Ag-Zn cells were on discharge and for discharge of the Cd micro fuel cells only while the Ag-Zn cells were on charge. This arrangement avoided the intercell leakage currents. All of these relays were operated by the same timer that controlled the Ag-Zn cells. All other conditions for this phase were identical to the prior phases except that the test was carried out with only seven assemblies instead of eight as one Ag-Zn cell was damaged in prior testing. Operation was carried out in this mode for an additional 115 hours during which three more Ag-Zn cells failed and were removed from test.

At this point, it was decided to shut down again and modify the circuit so as to completely eliminate the parallel charge arrangement of the Cd micro fuel cells. Instead of charging these micro fuel cells in parallel, it was decided to charge them separately as required. This greatly simplified the circuit as shown in Figure 11. The parallel charge lines leading to the Cd micro fuel cells as well as the entire transistor circuits were completely removed. This left only the basic Ag-Zn circuits and separate micro fuel cell circuits.

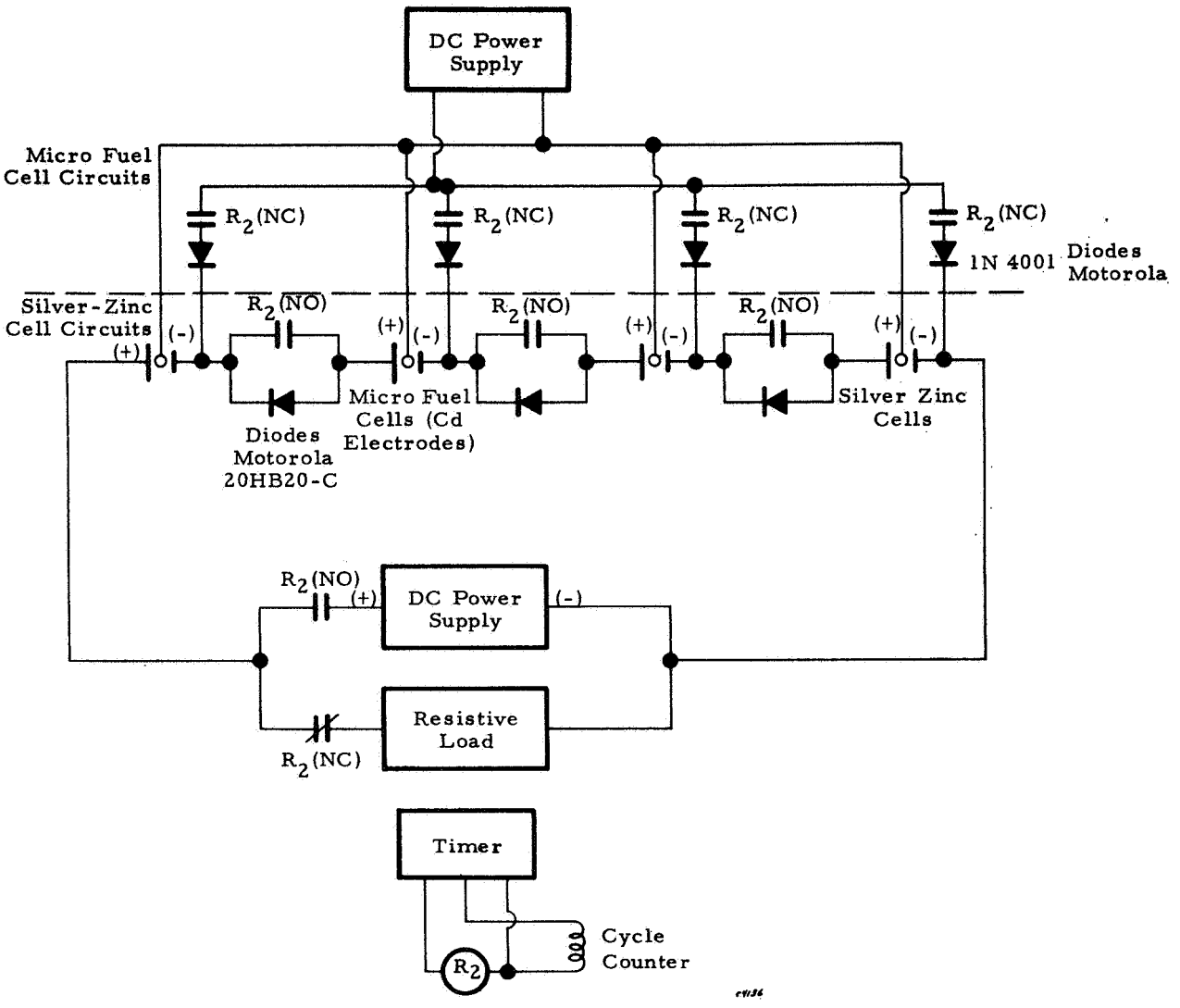


Figure 9. Modified Circuit Incorporating Diodes in Silver-Zinc Cell Discharge Circuit (90 Minute Regime)

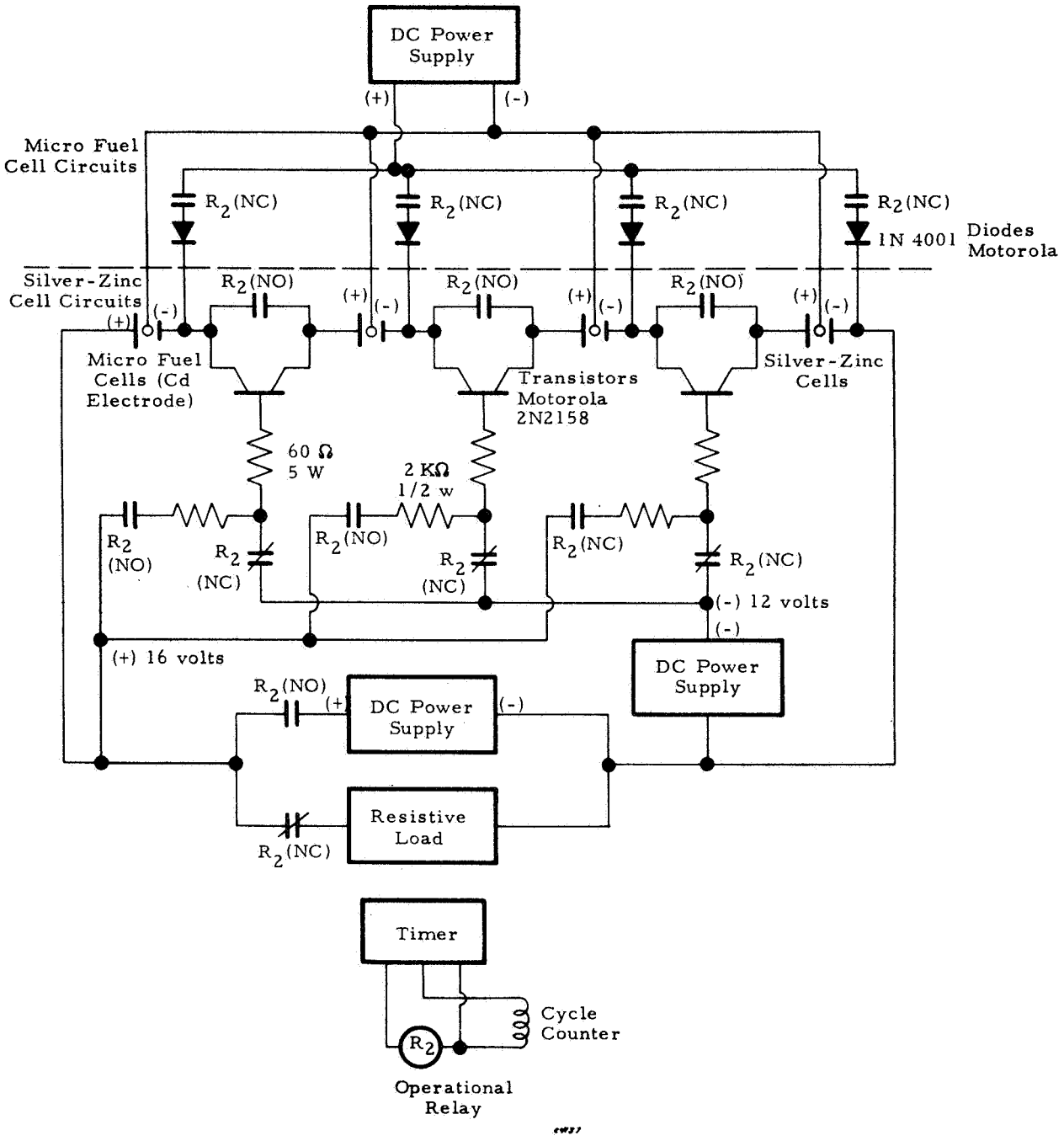


Figure 10. Modified Circuit Incorporating Power Transistors in Silver-Zinc Discharge Circuit (90 Minute Regime)

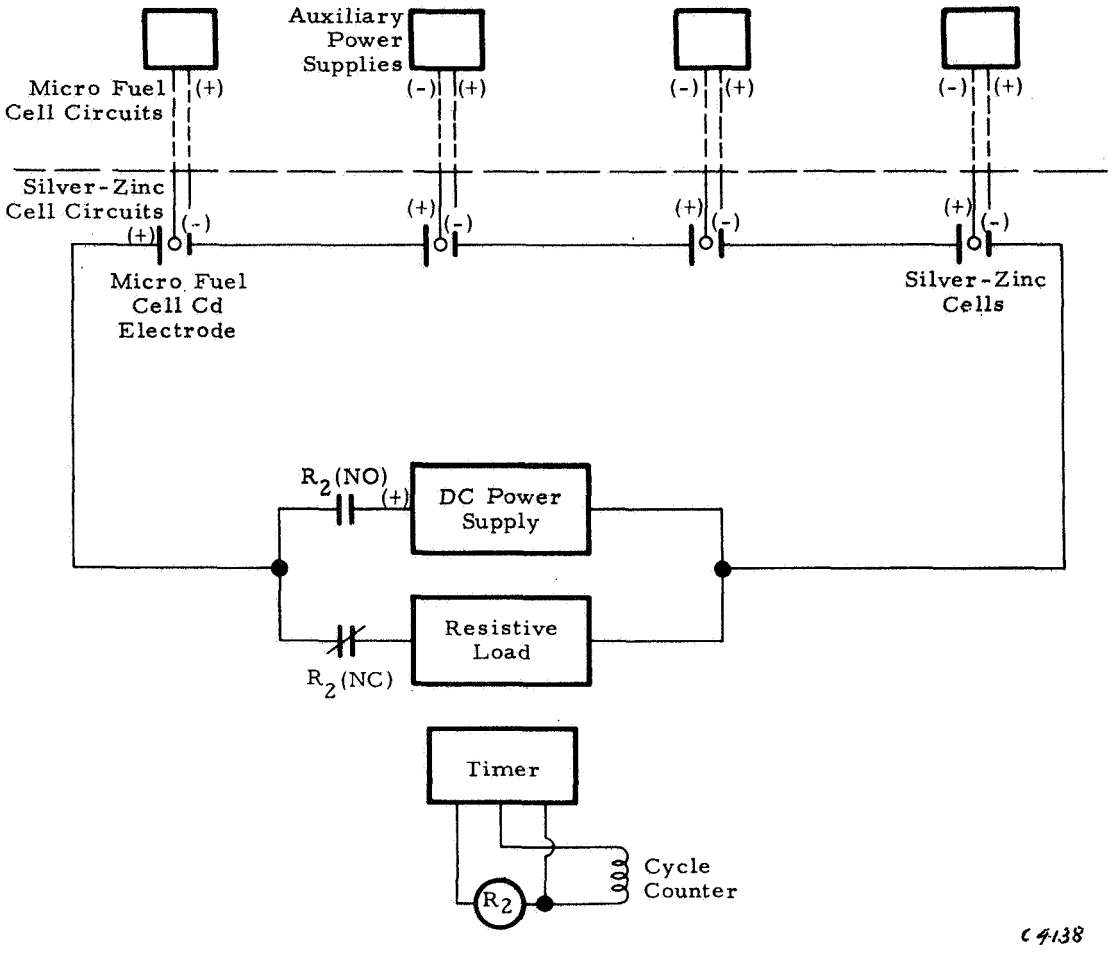


Figure 11. Final Circuit Employing Separate Charge Circuits for Cd Micro Fuel Cells (90 Minute Cycle Regime)

Operation in this final mode was carried out for an additional 455 cycles or 696 hours. One of the remaining four cells failed in the middle of this final period because an internal short circuit developed. The three remaining cells, however, performed satisfactorily until the end of the test.

Details of Stand Tests Under Phase I

Gassing studies at both room temperature and at 0°C were carried out with the AgO-Zn cells fully charged. Eight cells were tested consisting of four at 0°C and four at room temperature. Open circuit voltages and gassing rates of each of the cells were measured periodically. Room temperature varied from 24 to 26°C. The low temperature tests were carried out in a freezer set for and remaining at 0±1°C.

Details of Stand Tests Under Phase III

Stand tests were carried out on eight sealed assembles in a similar manner to the above. Four of these tests were at room temperature and four were at 0°C. All of the AgO-Zn cells were fully charged as above. Both the AgO and Cd micro fuel cells of each assembly were operated in the primary mode throughout. These were on direct short across their respective terminals. Currents in each of the micro fuel cell circuits were determined periodically by inserting a low range milliammeter in the lines. Open circuit voltages of the AgO-Zn cells were also read and recorded periodically.

The four assemblies on stand at room temperature were numbered #21 through 24. The four assemblies on stand at 0°C were numbered #9, 10, 19, and 20.

RESULTS OF PHASE I STUDIES

The objective of these studies was to obtain micro fuel cell design data for the sealed cell tests of Phase III. This was carried out by measuring the gassing characteristics of AgO-Zn cells under four different regimes and then calculating the appropriate fuel cell sizes to accommodate this gassing. Results of these studies are given below.

24-Hour Cycle Regime

Gassing and operating characteristics of eight cells on a 24-hour regime are given in Table I and in Figure 12. The test was run continuously for 81 cycles (81 days or 1944 hours) with the exception of a short term interruption caused by a power failure in the laboratory. Detailed test procedures were presented earlier.

In general, it may be stated that the cells on the 24-hour regime evolved extremely small quantities of gases. For example, the maximum amount of gas evolved from any one of the eight cells was only 222 cc for the indicated time. In addition, it should be pointed out that there were extended periods of a few weeks where some of these cells evolved almost no gases at all. In

TABLE I

GASSING CHARACTERISTICS OF EIGHT CELLS ON 24 HOUR CYCLE REGIME FOR 81 CYCLES (1944 HOURS)

Cell No.	Volume O_2 (cc)	Volume H_2 (cc)	Total Volume (cc)
9	38	2	40
10	79	13	92
11	143	19	162
12	148	8	156
13	192	27	219
14	189	21	210
15	218	4	222
16	191	4	195

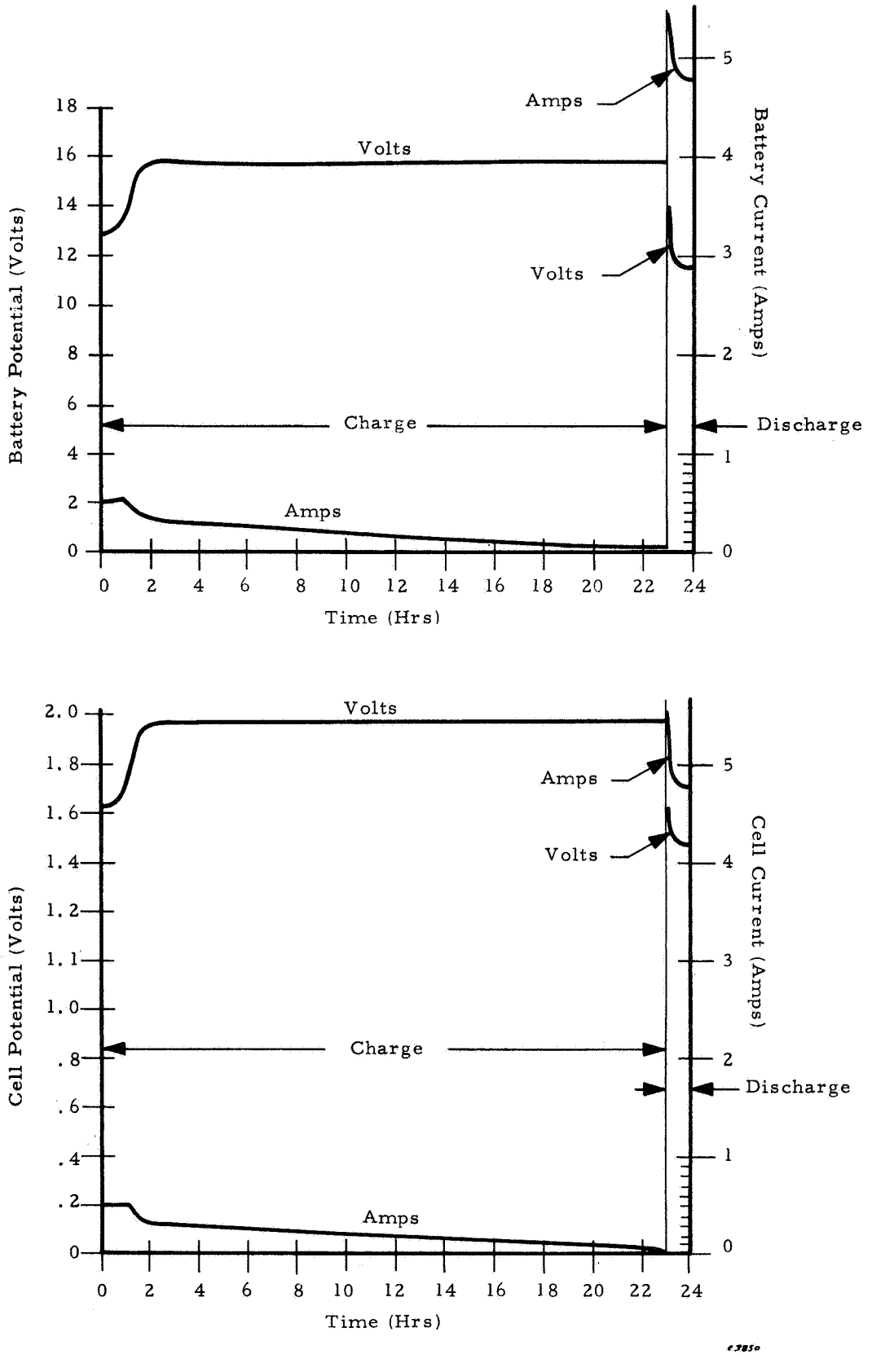


Figure 12. Typical Cycle Characteristics of Cells on 24-Hour Regime During Latter Stages (80 Cycles)

some cases, there were some signs of slow recombination as evidenced by a decrease in volume of gas within the cylinders.

A tabulation of the total amounts and composition of gases evolved from each of the eight cells for the complete cycle test is given in Table I. It is noted that the values range from a low of 40 cc in one cell to a high of 222 cc in another cell. Oxygen is the major constituent of the gases from all cells. In addition, it should be pointed out that most of this oxygen was evolved during the early stages of cycling after the initial formation cycles. The maximum amount of hydrogen evolved from any one cell was only 27 cc for the entire test.

Electrochemical performance of the eight cells was found to be quite uniform throughout the test. Typical characteristics of both a single cell and the stack of eight cells are given in Figure 12. Initial charge current was noted to hold constant at 500 mA for about 1 hour, and then drop sharply to a level near 350 mA. During the final 22 hours, there was a gradual decline in current to a level near 50 mA at the end of charge. Discharge current dropped sharply during the first 5 minutes of discharge from a level near 5.5 amperes to 4.7 amperes. Thereafter, the current held constant at 4.7 amperes to the end of the 1-hour discharge period. End-of-discharge voltages were relatively uniform throughout the test. Except for the first few cycles, the end-of-discharge voltages were all in the range of 1.44 to 1.47 volts. End-of-charge voltage did vary somewhat from cell to cell and for individual cells during the course of the test. There were times when it appeared that there might be signs of unbalance as the spread in end-of-charge voltages ranged from 1,90 to 2.01. These differences became smaller, however, during the course of cycling. During the latter stages of cycling the spread in end-of-charge voltages was only 1.94 volts to 1.99 volts.

There was only one cell that exhibited rather unique characteristics. This was Cell #9. End-of-charge voltage on this cell was consistently lower than all the others until near the end of the test and was in the range of 1.90 to 1.94. It was also noted that there were no gases evolved from this cell at all until near the end of the test when end-of-charge voltage reached 1.96 volts. Aside from this one cell, there are no other readily apparent correlations between electrical and gassing characteristics of the cells on this regime.

This test was interrupted for a short term after 1320 hours to conduct special trickle charge and capacity tests. The trickle charge was initiated at the end of a charge period and was continued for a period of 48 hours. Charge current continued to taper for the first 10 hours from a level near 30 ma to a level near 5 ma. During the last 38 hours an almost steady state current of 4 ma was maintained. End of charge voltages were 1.97 volts for all cells except one which was 1.92 volts. The maximum amount of gas evolved from any one cell was 44 cc and there were two cells that did not evolve any gas during this period. The maximum gassing rate from any one cell was 0.8 cc/hr at the end of the test.

The capacity test on these cells was carried out at the end of the trickle charge test. Discharge current was 5.2 amps at the beginning and 0.5 amps at the end. The first cell reached 1.0 volt after 4.63 hours at which point its output was 21.0 amp-hours. The last or eighth cell reached 1.0 volt approximately 1.5 hours later. During this final 1.5-hour period there were three cells that exhibited cell reversal to the extent of 0.1 volt. Only one of these cells evolved measureable quantities of gas (20 cc).

Micro fuel cell requirements for the AgO-Zn cells on this regime may be readily calculated on the basis of the measured gassing characteristics given in Table I. Results of these calculations are given in Table II. Required capacities of AgO cells to consume H_2 are very low with a maximum of only 64 mAh for 1944 hours. This corresponds to a required average current of only 33 μA and an AgO electrode of only 0.15 gram. Requirements of Cd cells to consume O_2 are somewhat higher than the above with a maximum of slightly over 1.0 Ah for 1944 hours. This corresponds to a maximum current of 0.53 mA and a Cd electrode with weight of 2.1 grams.

90-Minute Cycle Regime

Gassing and operating characteristics of eight cells on a 90-minute regime are given in Tables III and IV and Figures 13 and 14. This data has been divided into two parts. The first part is for the initial 880 cycles or 1320 hours during which the upper cutoff was 2.02 volts/cell. The second part is for the final 416 cycles or 624 hours during which the upper voltage cutoff was at the desired level of 2.05 volts/cell.

Table III gives the total amount and composition of gases evolved from the cells on this regime for the first 880 cycles. These data indicate that the gassing rates from the cells on this regime at a 2.02-volt cutoff are somewhat higher than the rates from the cells on the 24-hour regime which were at a 1.98-volt cutoff. However, the actual rates are still quite small, especially in comparison with the rates found on these cells at a 2.05-volt cutoff. The maximum amount of gas evolved from any one cell at the 2.02-volt cutoff was 268 cc for the 880 cycles. The minimum amount was 105 cc for one cell during this period. Again it will be noted that in all cases the major portion of the gas was oxygen. Most of this oxygen was found to be evolved periodically during a one or two day interval when end of charge voltage on a given cell approached 2.10 volts. Very little, if any, oxygen was evolved at other times (this is discussed below). Hydrogen was found to be evolved quite slowly and uniformly in these cells at rates in the range of 1.0 to 2.0 cc/day.

End-of-charge voltages of the cells on this regime were somewhat more erratic than the end-of-charge voltages of those cells on the 24-hour regime. There were intervals of one or two days during which the end-of-charge voltage of a given cell would progressively increase and then decrease each cycle from a level below 2.00 volts to a maximum near 2.10 volts, and then below 2.00 volts once again. Simultaneously there was a marked increase

TABLE II

MICRO FUEL CELL REQUIREMENTS FOR CELLS ON 24 HOUR CYCLE REGIME FOR 81 CYCLES OR 1944 HOURS

Cell No.	Required Capacity of Cd Cell (mah)	Required Average Current from Cd Cell (ma)	Required Capacity of AgO Cell (mah)	Required Average Current from AgO Cell (μ A)
9	181	0.09	5	3
10	375	0.19	31	16
11	770	0.40	45	23
12	740	0.38	19	10
13	910	0.47	64	33
14	900	0.46	50	25
15	1030	0.53	10	5
16	905	0.46	10	5

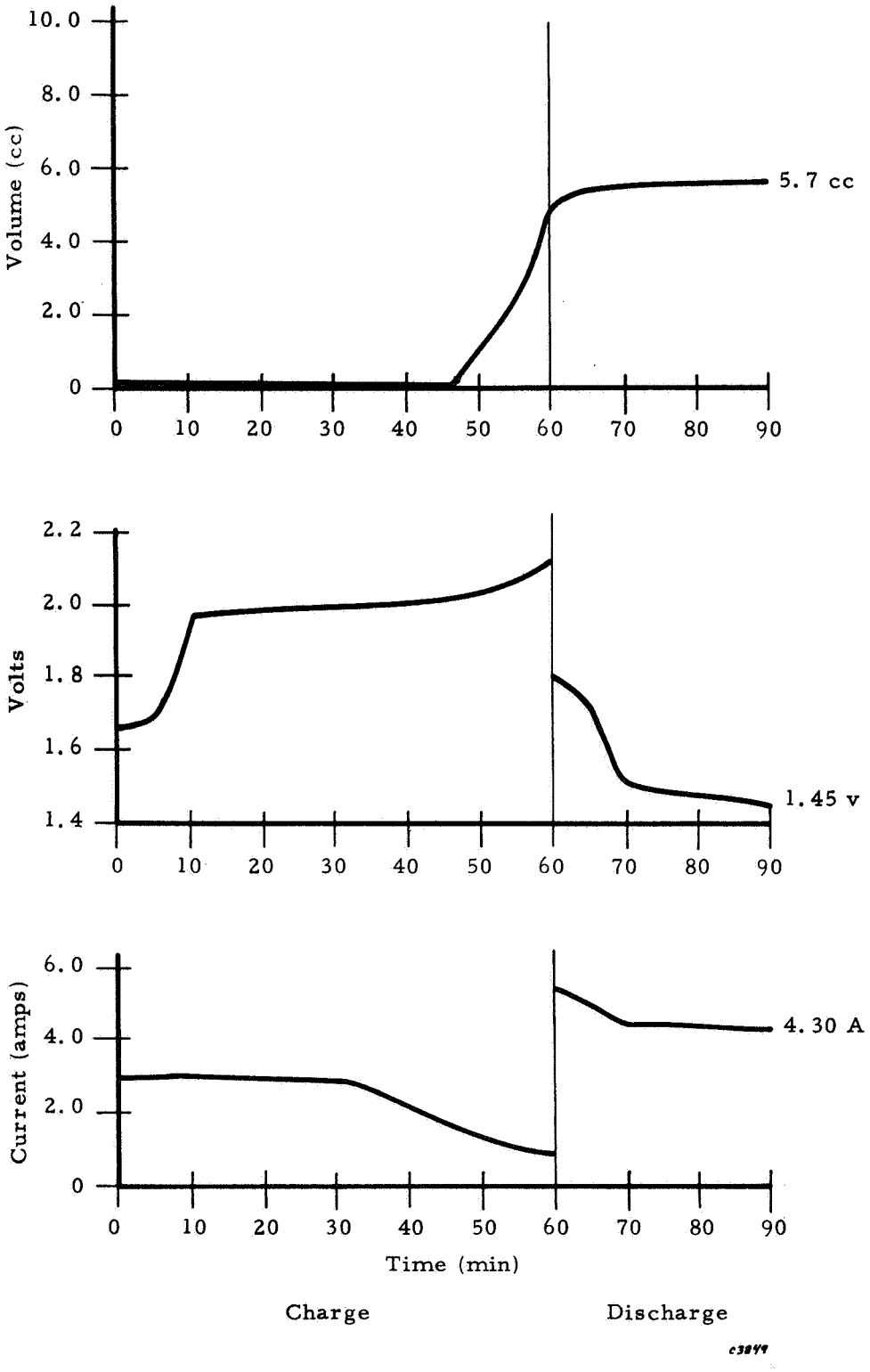


Figure 13. Typical Gassing Characteristics of a Cell on the 90 Minute Regime

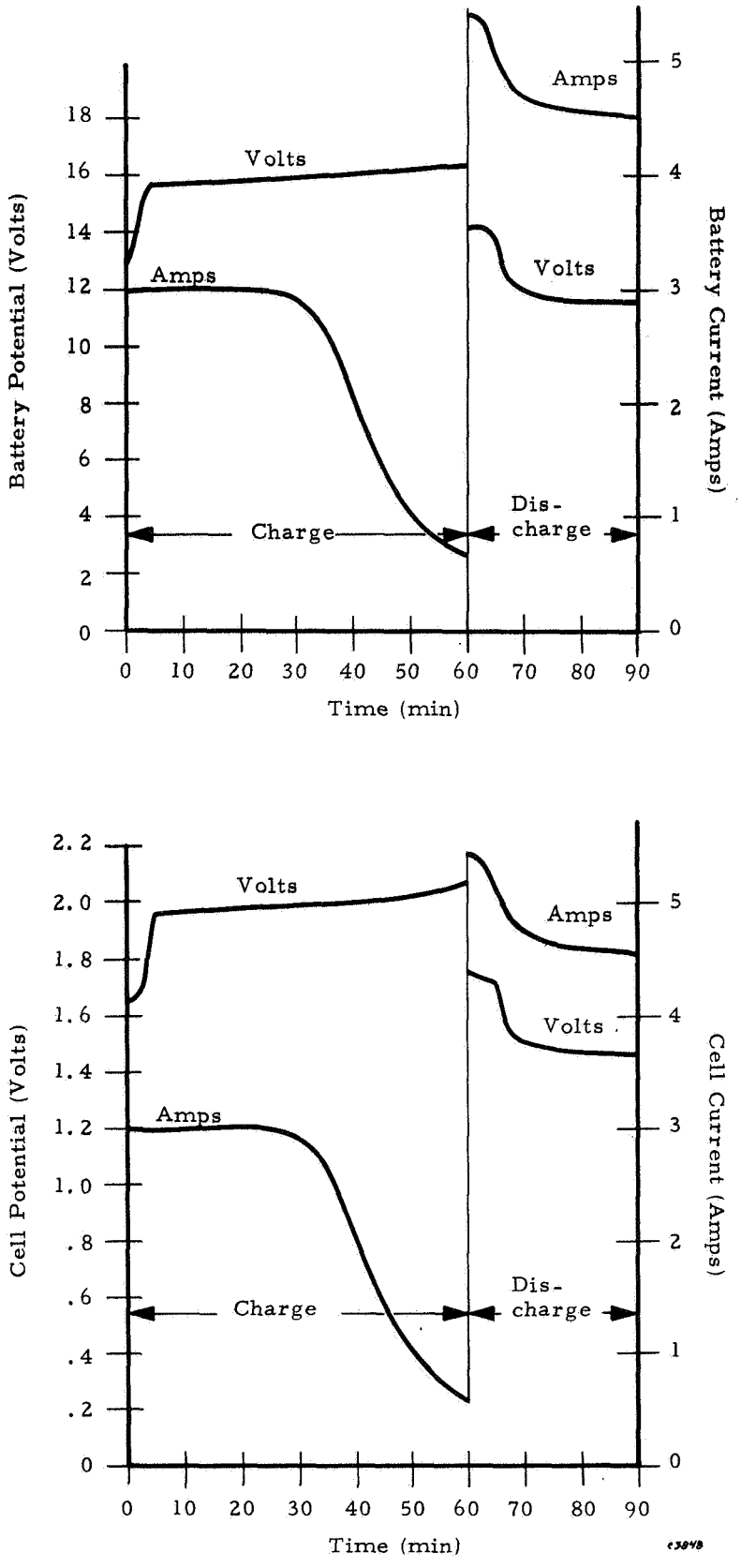


Figure 14. Typical Cycle Characteristics of Cells on 90-Minute Regime During Latter Stages (1250 cycles)

TABLE III

GASSING CHARACTERISTICS OF EIGHT CELLS ON 90 MINUTE CYCLE REGIME FOR FIRST 880 CYCLES OR 1320 HOURS

Cell No.	Volume O_2 (cc)	Volume H_2 (cc)	Total Volume (cc)
17	206	62	268
18	111	75	186
19	95	53	148
20	76	87	163
21	53	52	105
22	65	64	129
23	60	50	110
24	123	89	211

and then decrease in oxygen evolution. There was no apparent pattern to the occurrence of this phenomenon, but it did occur in all of the cells at least once during this interval. The maximum amount of oxygen evolved from a cell during these periods was about 100 cc/day. End-of-discharge voltages were quite uniform for all the cells during this period and were in the range of 1.44 to 1.48 volts.

Gassing data for these cells at the 2.05-volt cutoff for the remaining 416 cycles are given in Table IV. These data indicate a marked increase in overall gassing rate of all cells. The maximum additional amount of gas evolved from any one cell during the period was 2197 cc. As before, the major portion of this gas was found to be oxygen. Most of this was evolved at the end of a charge cycle on cells with voltages in excess of 2.05 volts. Figure 13 gives the gassing characteristic of such a cell for a typical cycle. Here it is noted that the first signs of gassing occur after approximately 48 minutes of the 60-minute charge period. Gassing rate and also cell voltage are noted to increase quite rapidly at this point and the current is noted to taper to lower levels. This trend continues until the end of the charge period when the gassing rate falls sharply. The total amount of gas evolved during this cycle was 5.7 cc. Other cells were noted to evolve larger quantities of gas during these periods with a maximum of approximately 11 cc per cycle. Although the average gassing rates in all the cells were much higher during this period, it should be pointed out that the rates were not consistently higher. As above, there were times when a given cell would exhibit very high rates and end-of-charge voltage for several cycles and then exhibit relatively low rates and end-of-charge voltage for subsequent cycles. No definite pattern to this phenomenon was noted, however, it did occur in each cell at least once during the final 416 cycles. The maximum rate of hydrogen evolution during this period (624 hours) was slightly over one cc per hour. This test was interrupted for a short term after 1320 hours to carry out special trickle charge and capacity tests. The trickle charge was initiated at the end of a charge period and was continued for a period of 45 hours. Charge current continued to taper for the first 24 hours from a level near 80 ma to a level near 40 ma. This final current was maintained for the final 21 hours. End of charge voltages were 2.02 to 2.03 volts for all cells. The maximum amount of gas evolved from any one cell was 541 cc during this period. All cells were gassing at relatively constant rates at the end of the test with rates ranging from 8.2 to 13.6 cc/hour. The capacity test on these cells was carried out at the end of the trickle charge test. Initial discharge current was 5.2 amps and final current was 1.3 amps. The first cell reached 1.0 volt after 4.50 hours at which point it had delivered 19.1 amp-hours. The last or eighth cell reached 1.0 volt after 5.55 hours. During this latter interval there was only one cell which exhibited reversal to the extent of -0.08 volts. Two cells evolved significant quantities of gas during this latter interval to the extent of 100 to 120 cc. All other cells exhibited little or no gassing throughout the capacity test.

Micro fuel cell requirements for the AgO-Zn cells on this regime were somewhat higher than the requirements for the same type of AgO-Zn cells on the 24-hour regime. A tabulation of these requirements is given in

TABLE IV

GASSING CHARACTERISTICS OF EIGHT CELLS ON 90 MINUTE CYCLE REGIME FOR LAST 416 CYCLES OR 624 HOURS

Cell No.	Volume O_2 (cc)	Volume H_2 (cc)	Total Volume (cc)
17	2057	533	2590
18	1339	93	1432
19	2197	476	2673
20	1392	106	1498
21	1127	12	1139
22	1823	237	2060
23	1942	696	2638
24	1247	241	1488

Tables V and VI. Required capacity of AgO cells to consume H_2 were moderate for the first 1320 hours at the 2.02 volt cutoff (see Table V). The maximum required capacity of an AgO cell for this period was 0.21 Ah. This requires an AgO cell which contains 0.49 gram AgO and delivers an average current of 0.16 mA. Maximum required capacity of a Cd cell for this period was 0.98 Ah. This would require a Cd cell which contains 2.0 grams Cd and delivers an average current of 0.74 mA. Micro fuel cell requirements for the last 624 hours at the 2.05 volt cutoff were much higher than at the 2.02 volt cutoff as indicated in Table VI. Maximum required capacity of an AgO cell for this period was 1.66 Ah. This calls for an AgO cell which contains 3.83 grams AgO and delivers an average current of 2.7 mA. The maximum required capacity of a Cd cell for this period was exceptionally high at 10.46 Ah. This would require a Cd cell which contains 21.8 grams Cd and delivers an average current of 16.5 mA.

These latter results signified that it would be impractical to attempt to design and operate a primary type Cd cell for this regime at a 2.05 volt cutoff. Size and weight requirements of such a Cd cell would be prohibitively large for the given size of AgO-Zn cell. The only feasible method of operating the Cd micro fuel cells appeared to be in the secondary mode with recharge. This mode was subsequently employed in tests of sealed assemblies in Phase III. The results did not appear to require secondary operation of the AgO cells over significant operating times. Therefore, it was decided to operate these cells in the primary mode at least in the early stages.

Stand at 0°C

No measurable quantities of gas were evolved from any of the four cells on stand at 0°C for the entire operating time of 1944 hours. These results signified that there were essentially no fuel cell requirements for this operating mode.

Stand at Room Temperature

Two of the four cells on stand at room temperature evolved small quantities of hydrogen for the first few weeks of stand at rates near 1cc/day. Thereafter, no measurable quantities of gases were evolved from these cells to the end of the test period of 1944 hours. No measurable quantities of gas were evolved from the other two cells at any time during this test period. These results signified that the only fuel cell requirements for the above test would have been small AgO cells with a capacity of only 50 milliampere-hours.

TABLE V

MICRO FUEL CELL REQUIREMENTS FOR CELLS ON 90 MINUTE CYCLE REGIME FOR FIRST 880 CYCLES OR 1320 HOURS

Cell No.	Required Capacity of CD Cell (AH)	Required Average Current from CD Cell (ma)	Required Capacity of AgO Cell (mah)	Required Average Current from AgO Cell (ma)
17	0.98	0.74	0.15	0.11
18	0.52	0.39	0.18	0.14
19	0.45	0.34	0.13	0.10
20	0.36	0.27	0.21	0.16
21	0.25	0.19	0.12	0.09
22	0.31	0.23	0.15	0.11
23	0.29	0.22	0.12	0.09
24	0.58	0.44	0.21	0.16

TABLE VI

MICRO FUEL CELL REQUIREMENTS FOR CELLS ON 90 MINUTE CYCLE REGIME FOR LAST 416 CYCLES OR 624 HOURS

Cell No.	Required Capacity of CD Cell (AH)	Required Average Current from CD Cell (ma)	Required Capacity of AgO Cell (mah)	Required Average Current from AgO Cell (ma)
17	9.80	15.7	1270	2.0
18	6.38	10.4	220	0.4
19	10.46	16.5	1130	1.8
20	6.64	10.6	250	0.4
21	5.42	8.7	30	0.05
22	8.73	14.0	570	0.9
23	9.25	14.8	1660	2.7
24	5.93	9.5	570	0.9

RESULTS OF PHASE II STUDIES

The objective of this investigation was to obtain pertinent design data on micro fuel cells for application in the sealed cell tests of Phase III. The work involved parametric studies on both AgO and Cd micro fuel cells under simulated battery gassing environments. A detailed description of the micro fuel cells and methods of testing them is given earlier. Results of these tests are given below.

Typical Operating Characteristics

All of the pertinent design data on the micro fuel cells can be derived from their particular polarization and cycle characteristics. Polarization data is used to determine rate of gas consumption and required charge voltages and cycle data is used to determine the total gas consumption capacity. Typical performance curves on both types of micro fuel cells are given in Figures 15 through 18 and are discussed below.

Figure 15 gives two sets of polarization data on an AgO micro fuel cell in a hydrogen atmosphere at 25°C. One set was obtained with the cell in the state of full charge and the second with the cell in the state of near complete discharge. Electrode area was 1.0 cm^2 and weight of Ag was 2.8 grams. Corresponding theoretical capacity was 1.2 Ah. Results indicated that polarization characteristics are markedly influenced by state of charge. When the cell is fully charged, it can deliver currents in excess of 200 mA/cm^2. For the 1.0 cm^2 cell, this corresponds to 200 mA or an equivalent H_2 consumption rate of 84 cc/hr. When the cell is nearly discharged, its maximum current declines to values near 100 mA/cm^2 and the corresponding H_2 rate to 42 cc H_2/hour. Inspection of Figure 15 also indicates that charge voltages of a fully charged cell are from 0.2 to 0.5 volt greater than those of a discharged cell depending on the current density. These differences are attributed not only to polarization phenomena but also to the two valence states of the silver cathode.

Figure 16 gives typical polarization data of a Cd micro fuel cell in an O_2 environment at 25°C. Electrode area was again 1.0 cm^2 and weight of Cd was 2.95 grams. Corresponding theoretical capacity was 1.4 Ah. Results again indicate that polarization characteristics are markedly influenced by state of charge of the cell. When fully charged, the Cd cell can deliver currents in excess of 200 mA/cm^2 and when fully discharged the maximum current drops to slightly less than 100 mA/cm^2. For a cell with 1.0 cm^2 electrodes these values correspond to O_2 consumption rates of 42 and 21 cc/hr, respectively. Required charge voltage of a fully charged cell can be as much as 0.5 volt greater than that of an uncharged cell depending upon the current. It is also interesting to note that the Cd cell exhibits much more polarization than the AgO cell at low current densities. This is attributed to the high activation polarization of the O_2 cathode of the Cd micro fuel cell.

The above type of polarization data proved quite useful in the design of micro fuel cells for the sealed cells of Phase III. The data permitted fairly accurate estimates of required electrode area which is a key factor of design.

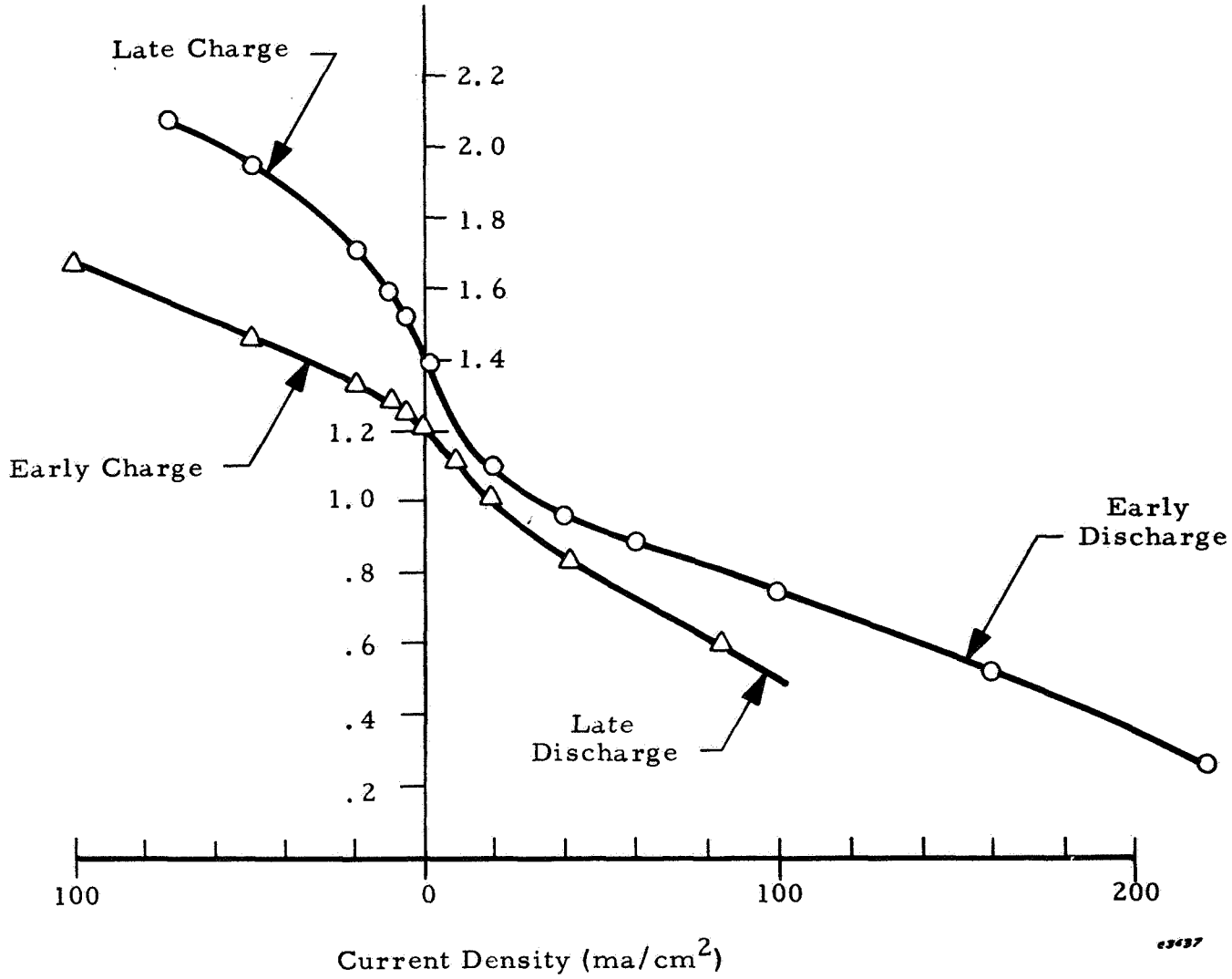


Figure 15. Polarization Characteristics of AgO - H_2 Micro Fuel Cells

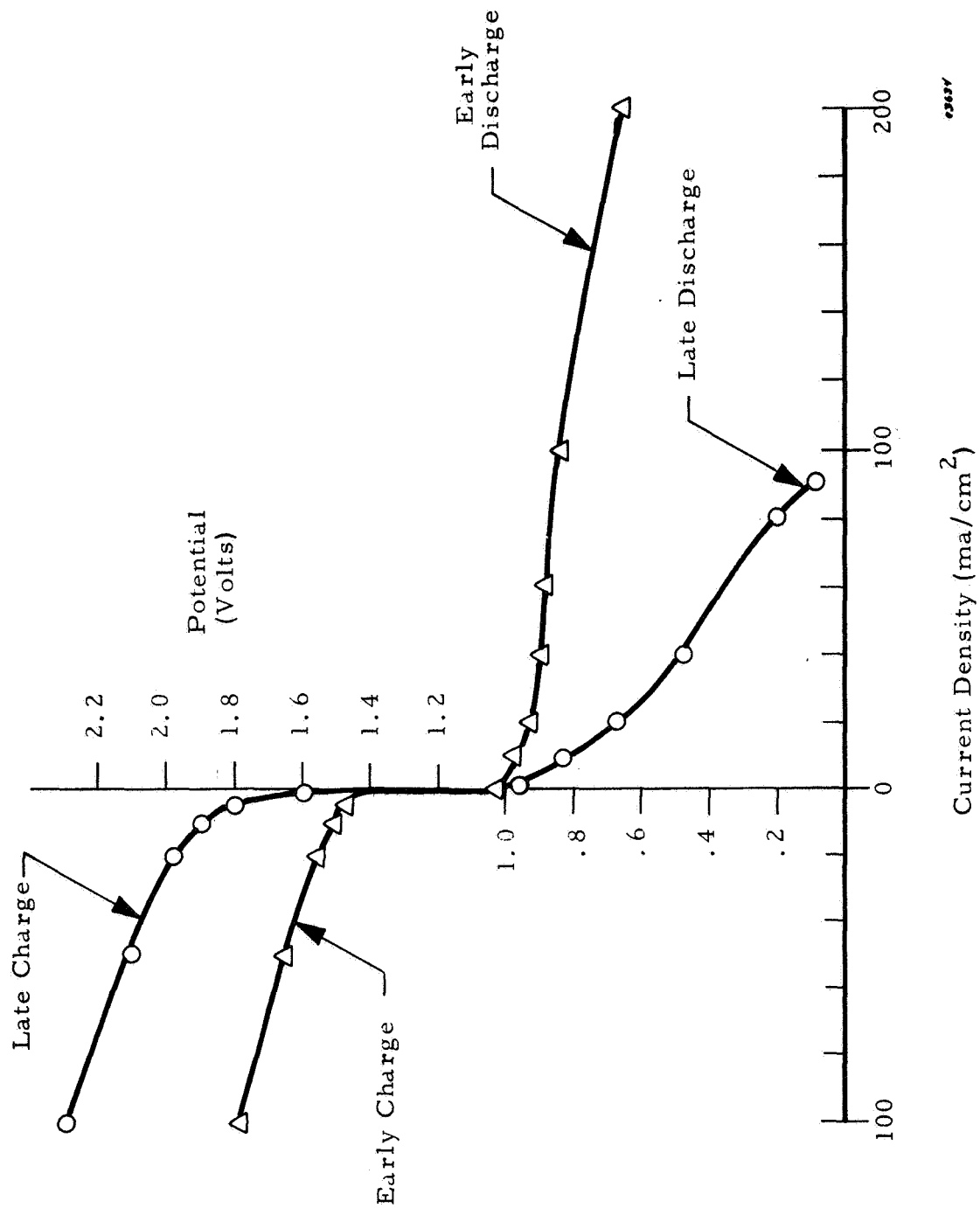


Figure 16. Polarized Characteristics of Cd-O_2 Micro Fuel Cells

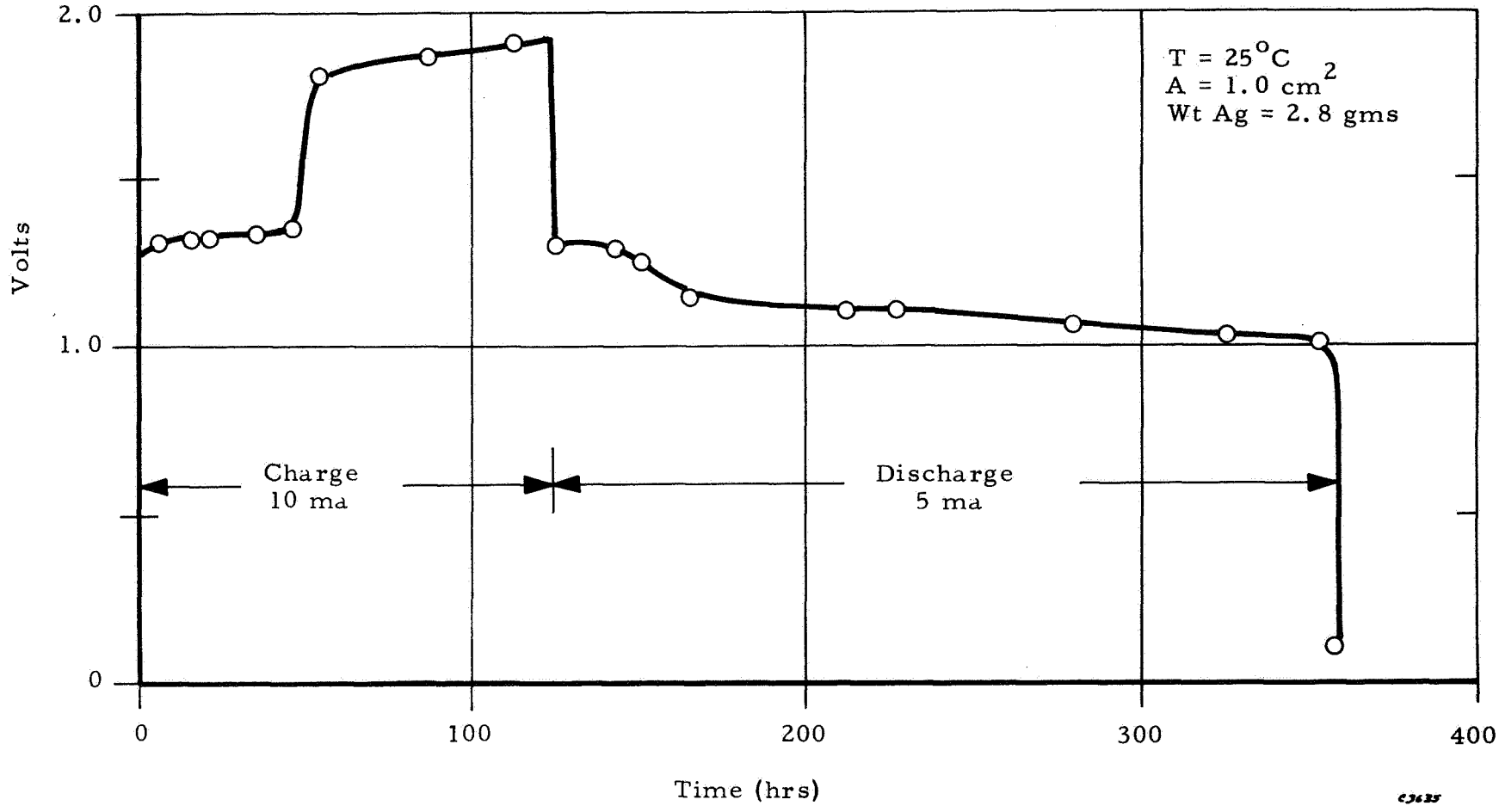


Figure 17. Cycle Characteristics of AgO-H_2 Micro Fuel Cells

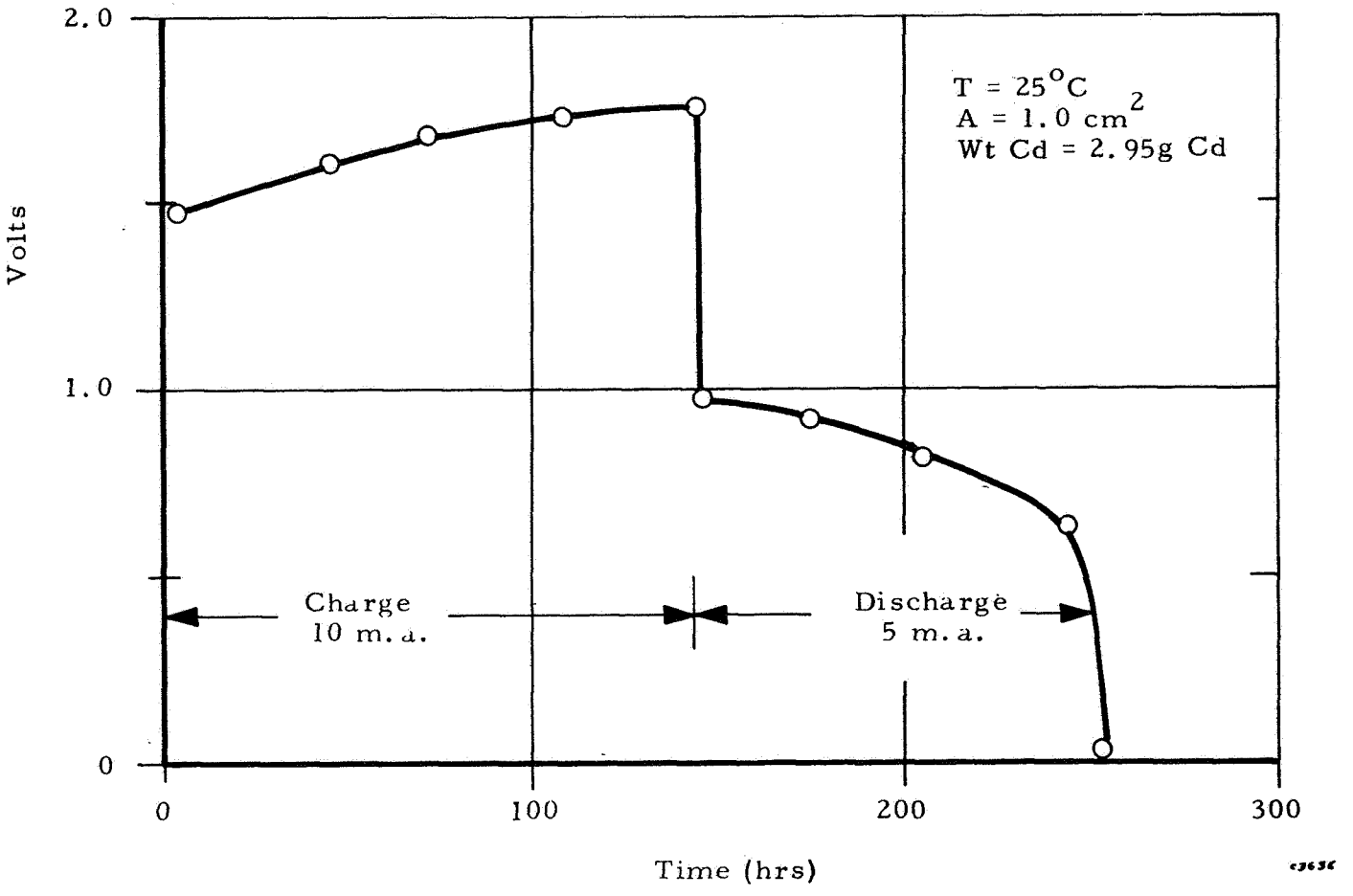


Figure 18. Cycle Characteristics of Cd-O_2 Micro Fuel Cells

Figure 17 gives the operating voltages of an AgO micro fuel cell during a complete charge-discharge cycle. Electrode area was again 1.0 cm^2 and weight of Ag was 2.8 grams as above. Charge was carried out for 138 hours at 10 mA to give an input of 1.38 Ah or 100% of theoretical based on weight of Ag. Discharge was carried out at 5 mA to 0 volt cutoff. The observed voltage traces as shown in Figure 17 are found to be quite similar to those of similar cells with AgO cathodes. Two voltage plateaus are noted for both charge and discharge. These correspond to the two valence states of the silver cathode. The most significant result of the above is the discharge time and corresponding output. Here it is noted that the cell delivered a current of 5 mA for 204 hours for an output of 1020 mAh. This corresponds to a consumption of 427 cc H_2 and an efficiency of 74%, based on weight of Ag.

Figure 18 gives the characteristic voltage curves for a complete cycle on a Cd micro fuel cell in an O_2 environment at 25°C. Electrode area was again 1.0 cm^2 and weight of Cd was 2.95 grams as above. Charge was carried out at 10 mA for 145 hours to give 1.45 Ah or 100% of theoretical input based on weight of Cd. Discharge was carried out at 5 mA to 0 volt cutoff. The observed voltage traces were somewhat different from those of the AgO cell above. Charge voltage was noted to rise gradually throughout the charge period and discharge voltage was noted to decline throughout the discharge period. The most significant point of the above, however, is the discharge time and corresponding output. In this case, it is noted that the cell delivered an output of 5 mA for 112 hours or 560 mAh. This corresponded to an O_2 consumption of 117 cc O_2 and a corresponding efficiency of 39%.

This type of data was used to determine the required thickness and weight of the solid micro fuel cell electrodes for the Phase III tests.

Effect of Electrode Thickness

Although theory predicts that capacity of an electrode should be directly proportional to its thickness, this principle does not apply in all cases. Exceptions to this rule are especially noted for very thick electrodes discharged at high current. Capacity and efficiency are usually quite low in these cases. Based on the above known trends, it was decided to obtain quantitative data for the effect of thickness on capacity of both AgO and Cd cells. The results obtained are given in Tables VII and VIII.

Perhaps the most striking results are those obtained on the cell with the thickest AgO electrode. The results indicate that this cell, containing a cylindrical AgO electrode with dimensions of 1.12 cm diameter by 1.27 cm thick, delivered 2.30 Ah, or 67% of its theoretical capacity. The operating current and time were 5 mA (5 mA/cm^2), and 460 hours, respectively. The volume of hydrogen consumed was 966 cm^3. Efficiency of the thinner AgO electrodes appears to be somewhat higher. These results indicate a trend toward improved efficiency with decreased electrode thickness. A general conclusion that may be reached is that capacity of an AgO cell can be increased by increasing the thickness of the AgO electrode, but the increase in capacity is not directly proportional to thickness.

TABLE VII

EFFECT OF SILVER ELECTRODE THICKNESS ON CAPACITY AND EFFICIENCY OF AgO-H_2 MICRO FUEL CELL

Thickness (cm)	Weight Ag (gms)	Theoretical Capacity (Ah)	Discharge Current (mA)	Discharge Time (hrs)	Output (Ah)	Efficiency (%)
0.191	1.0	0.49	5.0	76	0.38	77
0.533	2.8	1.38	5.0	206	1.02	74
1.270	7.0	3.45	5.0	460	2.30	67

TABLE VIII

EFFECT OF CADMIUM ELECTRODE THICKNESS ON CAPACITY AND EFFICIENCY OF Cd-O_2 MICRO FUEL CELL

Thickness (cm)	Weight Cd (gms)	Theoretical Capacity (Ah)	Discharge Current (mA)	Discharge Time (hrs)	Output (Ah)	Efficiency (%)
0.191	0.76	0.36	5.0	27	0.13	36
0.533	3.0	1.43	5.0	110	0.55	38
1.270	5.0	2.43	5.0	216	1.08	43

Efficiency of the Cd cells, however, is noted to be almost independent of electrode thickness over the indicated ranges. In this case, the capacity is directly proportional to thickness of the Cd electrode.

Effect of Discharge Rate

Since the capacity of most electrochemical cells is usually dependent upon discharge rate, it was thought advisable to determine the extent to which this relationship is applicable to micro fuel cells. Results of a series of runs to establish the effect of discharge rate are given in Tables IX and X. Examination of these data indicates that there is a trend toward decreased capacity and efficiency of the AgO cell with increase in current density over the range of 2 to 50 mA/cm^2. At the lower currents, these cells can deliver almost 90% of their theoretical capacity while at the higher currents, they can effectively deliver only about 60% of theoretical. In cadmium cells, however, there is no such marked trend toward decreased efficiency with increased discharge current in the range of 2 to 50 mA/cm^2. Capacity and efficiency of this cell are essentially independent of discharge rate in this range. Efficiency of the Cd cells at all of the indicated current levels is around 35%.

Effect of Charge Rate

Two series of tests were carried out on Cd and AgO micro fuel cells to determine the effect of charge current density on capacity and efficiency. Results of these tests are given in Table XI for Cd cells run on oxygen and Table XII for AgO cells run on hydrogen. Electrode areas in both cases were 1.0 cm^2 so that the indicated currents in mA are actually current densities, i.e., mA/cm^2. The Cd electrodes employed here weighed 5.7 grams each and had a theoretical capacity of 2.5 Ah. The AgO electrodes weighed 3.2 gms and had a theoretical capacity of 1.4 Ah.

Results on both series of tests indicated a definite trend toward reduced capacity and efficiency with increased charge current. Output and efficiency of the Cd cells, for example, are noted to be reduced by almost 50% as charge current is increased from 10 to 100 mA/cm^2. Similarly, the output and efficiency of AgO cells are noted to be appreciably reduced as charge current is increased over the same range. The cause for these trends is attributed to inefficiencies in the charging process at high current densities. At these high rates and corresponding high voltages, a significant portion of the input current results in gas evolution at the micro fuel cell electrodes rather than the desired electrochemical reaction. This was substantiated in the high rate charge of the Cd cells where the effluent gas was found to contain appreciable amounts of hydrogen.

Operational Life

Continuous cyclical operation was carried out on several of the AgO and Cd micro fuel cells for two months. Very little, if any, degradation in

TABLE IX

EFFECT OF DISCHARGE CURRENT ON CAPACITY AND EFFICIENCY OF $AgO-H_2$ MICRO FUEL CELLS

Discharge Current (mA)	Thickness (cm)	Weight Ag (gms)	Theoretical Capacity (Ah)	Discharge Time (hrs)	Output (Ah)	Efficiency (%)
2	0.533	2.8	1.38	482	0.97	70
5	0.533	2.8	1.38	206	1.02	74
50	0.533	2.8	1.38	16	0.81	58

TABLE X

EFFECT OF DISCHARGE CURRENT ON CAPACITY AND EFFICIENCY OF $Cd-O_2$ MICRO FUEL CELLS

Discharge Current (mA)	Thickness (cm)	Weight Cd (gms)	Theoretical Capacity (Ah)	Discharge Time (hrs)	Output (Ah)	Efficiency (%)
2	0.533	3.0	1.43	285	0.57	40
5	0.533	3.0	1.43	112	0.56	39
10	0.533	3.0	1.43	53	0.53	37
20	0.533	3.0	1.43	25	0.50	35
50	0.533	3.0	1.43	10	0.50	35

TABLE XI

EFFECT OF CHARGE RATE ON CAPACITY AND EFFICIENCY OF CD MICRO FUEL CELLS

Charge Current (ma)	Discharge Current (ma)	Output (mah)	Efficiency (%)
10	5	1250	50
20	5	1083	43
50	5	919	37
100	5	668	27

TABLE XII

EFFECT OF CHARGE RATE ON CAPACITY AND EFFICIENCY OF AgO MICRO FUEL CELLS

Charge Current (ma)	Discharge Current (ma)	Output (mah)	Efficiency (%)
10	5	1020	74
20	5	900	65
50	5	635	46
100	5	600	43

capacity was noted during this period. Some cell failures did occur during this period on both types of micro fuel cells. The causes for these failures were established and are not considered critical. One of these was excessive drying caused by accidental overcharge or excessive gas flow rates. Both of these causes are associated with the method of test and would not apply to sealed battery tests. Other causes for failure have been found to be purely mechanical and can be eliminated entirely with rigid inspection procedures. It is also worthwhile to point out that one AgO micro fuel cell that is similar in design to the type used on this program was successfully operated for over 4000 hours. This has included 22 long charge-discharge cycles at 100% depth. The cell maintained 70% of its original capacity of 1.0 Ah during this period.

RESULTS OF PHASE III STUDIES

The objective of this phase of the program was to employ the results of Phase I and Phase II studies in the fabrication and test of sealed composite assemblies. The scope of the work involved fabrication and test of 24 composite assemblies under the four different operating modes as described previously. Results of these tests are given below.

24-Hour Cycle Test

This was the most extensive and perhaps the most significant of the four tests as it demonstrated long term functionality of a group of sealed composite assemblies operated in series. This involved a continuous test on eight series connected assemblies for 158 days on a 24-hour regime. An overall summary of the test is given in Table XIII and specific details are given in Table XIV and Figures 19 and 20.

Referring to Table XIII, it will be noted that the total operating time was 3792 hours. All but one of the assemblies performed satisfactorily during this period and was in good working order at the end. Final capacity tests at the end revealed that three of the AgO-Zn cells had maintained essentially all of their original capacity (>21 Ah). The one assembly that did not operate until this point was removed during the latter stages (after 128 cycles) because an internal short circuit developed. Effectiveness of the micro fuel cells is demonstrated quite well by the gas consumption and pressure data of Table XIII. Here it is noted that the maximum pressure developed in any assembly was only 0.841 Kg/cm^2 gage (12 psig) during the complete test. This compares quite favorably with the estimated maximum pressure of 137.5 Kg/cm^2 gage (1956 psig) that would have been developed without the use of micro fuel cells.

Electrical characteristics of the AgO-Zn cells were found to be relatively uniform and constant within the indicated ranges of Table XIII. The only exception was Assembly #13 which developed an internal short as described above. Operating voltages of this cell began to degrade after 100 cycles and reached 1.0 volt at the end of the 128th discharge period, when it was removed from the stack. The overall range in voltages for all other cells was 1.92 to

TABLE XIII

OVERALL SUMMARY OF CELLS ON 24-HOUR CYCLE REGIME

1.	Number of cells *	8 cells
2.	Total number of cycles	158 cycles
3.	Total operating time	3792 hours
4.	End of charge voltage range	1.92 - 2.08 volts
5.	End of discharge voltage range	1.44 - 1.62 volts
6.	End of charge current range	3 - 150 mA
7.	Discharge current range	4.4 - 5.6 amps
8.	Maximum pressure in a cell	0.841 Kg/cm^2 gage (12 psig)
9.	Output range of Cd cells	0 - 19 mA
10.	Output range of AgO cells	0 - 1.2 mA
11.	Maximum H_2 consumed in a cell	113 cc H_2
12.	Maximum H_2 pressure in a cell without AgO micro fuel cell **	7.8 Kg/cm^2 (111 psi)
13.	Maximum O_2 consumed in a cell	1870 cc O_2
14.	Maximum O_2 pressure in a cell without Cd micro fuel cell **	128.5 Kg/cm^2 (1830 psi)
15.	Maximum total pressure without AgO or Cd micro fuel cells **	137.5 Kg/cm^2 gage (1956 psig)

* One of the eight cells was removed from test after 128 cycles so that only seven cells completed the indicated number of cycles.

** These are estimated pressures that would be developed in Assembly #15 without micro fuel cells after 3792 hours on the assumption that there is no chemical recombination of gases.

TABLE XIV

TYPICAL DAILY SUMMARY REPORT OF ASSEMBLIES
ON 24-HOUR CYCLE REGIME (CYCLE #30)

Assembly Number	End Charge Voltage (volts)	End Discharge Voltage (volts)	Maximum Pressure Kg/cm^2 Gage	Output AgO Cell at End of Discharge (mA)	Output Cd Cell Early Charge (mA)	Output Cd Cell at End Charge (mA)
11	2.00	1.44	0	0.03	0.3	4.0
12	1.97	1.44	0	0.04	2.2	2.7
13	2.00	1.44	0	0.03	0.1	7.0
14	2.00	1.45	0.1	0.03	0.3	1.5
15	2.00	1.45	0	0.10	0.1	8.0
16	1.98	1.45	0	0.00	0.0	0.8
17	2.00	1.45	0	0.20	0.2	3.5
18	2 00	1.44	0	1.10	1.1	2.9

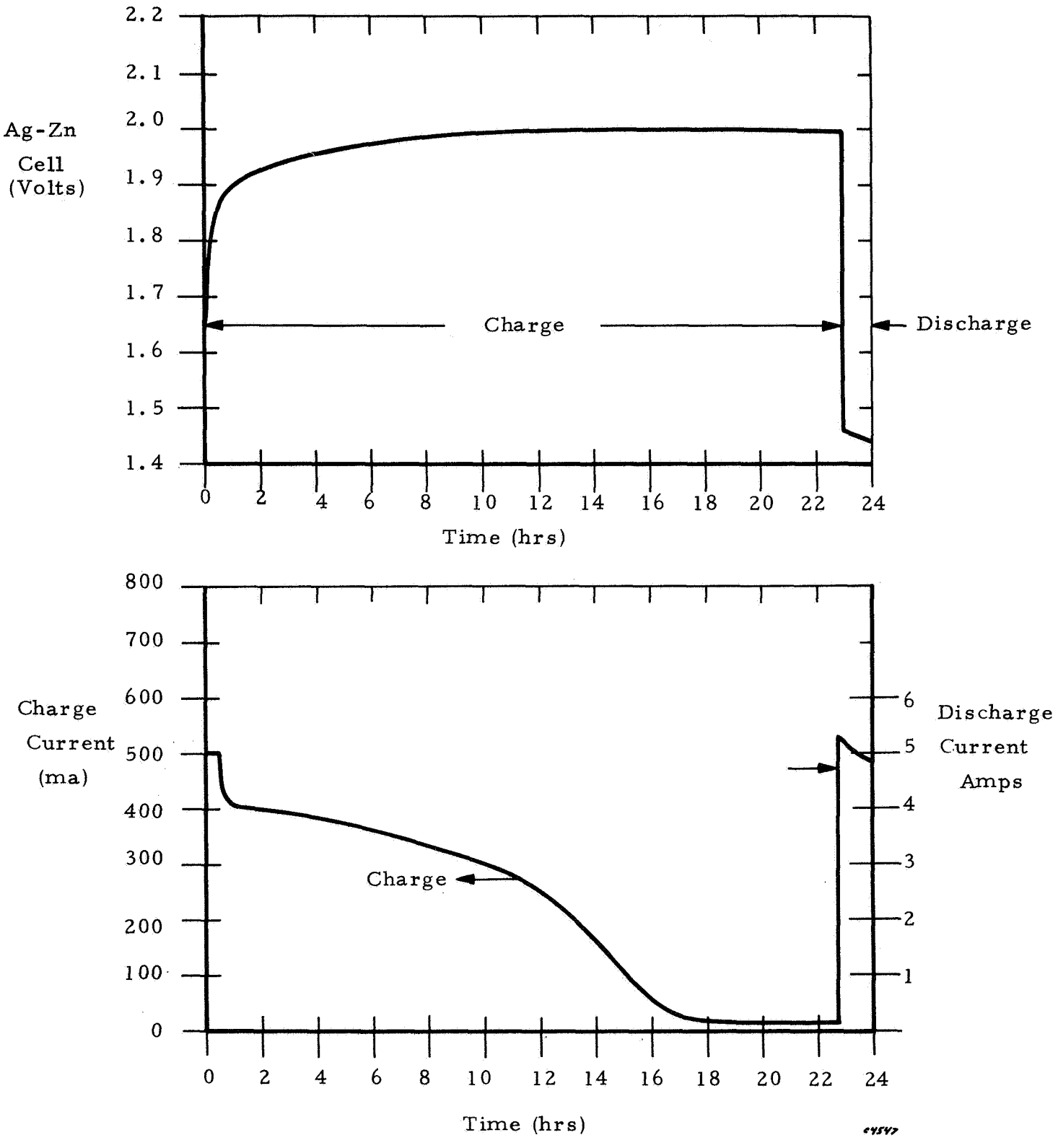
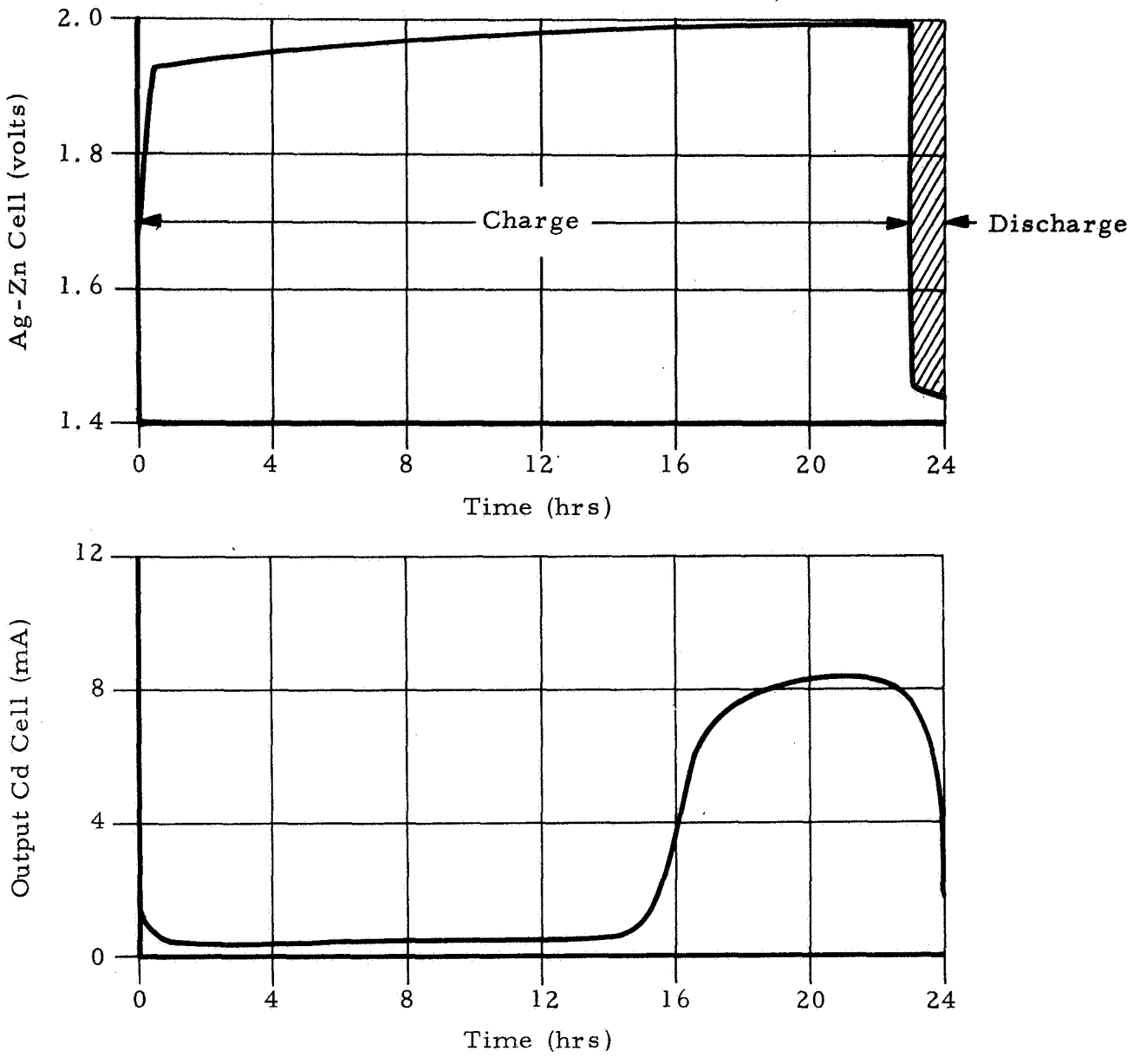


Figure 19. Typical Voltage and Current Profile of Cells on 24-hour Cycle Regime.



NOTE: Internal pressure in assembly was below 1 atm during entire period shown.

Figure 20. Characteristics of Cd Micro Fuel Cell During Cycle on 24-Hour Regime

2.10 volts for the end of charge and 1.44 to 1.62 volts for the end of discharge. Typical voltage and current profiles of an assembly for one complete cycle are given in Figure 19. The charge voltage is noted to start at 1.65 volts and rise rapidly to a level slightly above 1.90 volts. For the remaining 23 hours of charge, the voltage is noted to rise gradually to a level near 2.00 volts. Discharge voltage is noted to start at 1.45 volts and to decline only slightly to 1.44 volts at the end of the 1-hour discharge period. Charge current is noted to start at 500 mA and then drop sharply to 400 mA after 15 minutes. During the next 18 hours of charge, the current is noted to taper to 20 mA and remain at this level to the end of the charge period. Discharge current is noted to be slightly higher than 5 amperes at the start and slightly below this level at the end of discharge. These voltage and current profiles were typical of those for all the assemblies throughout the test. Some variations were noted among the cells for a given cycle and for a given cell from cycle to cycle. The overall variations, however, were within the ranges given in Table XIII.

Ampere-hour balances were performed periodically on input and output of the AgO-Zn cells. Results indicated cycling efficiencies of at least 95% throughout most of the test.

Internal pressures of all the assemblies were usually quite low and at a level less than 0.352 Kg/cm^2 gage (5 psig) throughout the test. Those assemblies which did exhibit positive pressures did so in a cyclical manner in accordance with the cycle regime. Maximum pressures occurred at the end of a given charge period and minimum pressure occurred shortly after the subsequent discharge period. There were a few periods lasting for one or two days during which the internal pressures of some assemblies reached higher values to 0.841 Kg/cm^2 gage (12 psig). This was most pronounced when Assembly #13 was beginning to degrade and caused unbalance among the other assemblies.

Case temperatures of the assemblies were found to be essentially the same as, and at most not more than, 1°C above room temperature. No measurable variations in temperature were noted among the cells or on a given cell during the course of a cycle.

Outputs of the AgO micro fuel cells were found to be relatively constant and low throughout the test in the range of 0.02 to 1.0 mA. Variation among cells for a given cycle are given in Table XIV. Outputs did vary within this range but not in any recognizable pattern. These results signified low and continuous H_2 rates in the range of 0.008 to 0.021 cc/hr. One exception to the above involved the AgO cell on Assembly #15. Output of this AgO cell was noted to increase on occasion to higher levels with a maximum of 1.2 mA. These periods began after 45 cycles and usually lasted for 1 or 2 days. On other occasions, the output was in the lower range indicated above. This result signified occasional periods of increased H_2 rates to 0.5 cc/hr. No correlation could be made between these periods of increased H_2 rates and other parameters. It was noted, however, that this particular assembly also evolved the most oxygen as indicated by its Cd micro fuel cell output.

Outputs of the Cd micro fuel cells were generally somewhat higher than those of the AgO cells and were found to vary in accordance with the charge

voltages of their respective assemblies. Those assemblies with higher end of charge voltages at 2.00 volts and above exhibited the highest output from their Cd cells. Those assemblies with lower end of charge voltages at 1.98 volts or less exhibited much lower and sometimes no output from their Cd cells. The maximum output from any given Cd cell was 19 mA throughout the test. Variation in Cd cell output during the course of a cycle is given in Figure 20 for an assembly with a moderately high end of charge voltage near 2.00 volts. During the first 15 hours of charge, the current is noted to be quite low and at a level near 0.5 mA. Shortly thereafter, the current is noted to increase quite sharply and then maintain an output of 8 mA for the remainder of the charge period. Voltage of the AgO-Zn cell is noted to simultaneously approach 2.00 volts during the later stages of charge. During the subsequent discharge period, the output is noted to decline once again to below 1.0 mA at the beginning of the following charge period. These results signify low O_2 rates near 0.1 cc/hr for the first 15 hours of charge and somewhat higher rates near 1.6 cc/hour for the last 8 hours of charge. Total O_2 consumption for the complete cycle can be calculated by integrating the current-time trace of Figure 20 and then converting to the equivalent amount of O_2. Results during this particular cycle indicate an output of 60 mAh or an equivalent of 12.6 cc of O_2.

The Cd micro fuel cells were operated in the primary mode for the first 25 cycles or 600 hours. At this point, however, it was noted that output of some of the Cd cells was beginning to degrade even though the voltages of their respective assemblies were near 2.0 volts. This indicated that the Cd cells were approaching the state of complete discharge. Inspection of the current-time output curves indicated that this was indeed the case. It was therefore decided to begin applying a charge to these Cd cells. Charge was applied periodically to these and other Cd cells as required throughout the remainder of the test period. The maximum input to any given Cd cell was 6.95 Ah, obtained for Cd cell of Assembly #15. This level of input was in accord with the overall ampere-hour balance on this Cd cell as it had an initial capacity near 2 Ah and had consumed 8.90 Ah equivalent of oxygen as explained below. This result also signified that the fuel cell was effectively recharged 3-1/2 times during this test.

Effectiveness of the micro fuel cells can be demonstrated best by calculating their total gas consumption and corresponding reduction of internal pressure. For the sake of this discussion, we will examine the most extreme case which is Assembly #15. As indicated above, this assembly evolved somewhat more O_2 and H_2 than any of the others. Integration of the fuel cell current output curves on this assembly revealed that its AgO cell had delivered 106 mAh and its Cd cell had delivered 8.90 Ah. These values correspond to gas volumes of 113 cc H_2 and 1870 cc O_2 respectively as shown in Table XIII. With an estimated free volume of 15 cc inside this size assembly, these volumes of gases would have caused pressure rise of 7.8 Kg/cm^2 (111 psi) for H_2 and 128.5 Kg/cm^2 (1830 psi) for O_2. Final gage pressure would then have been 137.5 Kg/cm^2 gage (1956 psig). It should be pointed out, however, that these estimates may be somewhat high (especially for O_2) as they do not consider the chemical recombination of these gases with the AgO-Zn electrodes. Regardless of this assumption, however, the results do quite clearly demonstrate the pressure relief capabilities of the micro fuel cells.

Finally, it is interesting to compare the measured fuel cell currents in this test with the estimated required currents which were calculated on the basis of the gassing data of Phase I. Results did indicate a fair correspondence between the two. For example, we might again examine the most extreme case which was assembly #15. Average output of the AgO cell on this assembly was 28 μA and average output of its Cd cell was 2.3 mA. (These values were obtained by dividing the measured output of the micro fuel cells by the total operating time.) Comparison of these currents with the estimates of Phase I (see Table II) indicates a fairly good correspondence. Current of the AgO cell was well within the range of the estimated AgO currents from the eight cells of Phase I (3 to 33 μA). Current of the Cd cell was somewhat higher than the corresponding estimated currents of Phase I, but was in the same order of magnitude. Average currents of the other Cd cells of Phase III corresponded more closely with the estimates of Phase I. These comparisons serve as a good check on the accuracy of the actual gassing rates of these cells on this regime. The results also illustrate that a micro fuel cell can be reliably designed to accommodate given gassing rates in a AgO-Zn cell.

90-Minute Cycle Regime

Initial phases of this test gave negative results in regard to performance of the sealed composite assemblies. Signs of rapid deterioration of the AgO-Zn cells were noted almost from the start. The major source of this problem was found to be the parallel charge circuit for the Cd micro fuel cells. Only when this charge circuit was removed did the test generate long term positive results.

The test was carried out in four different modes. Each of these differed from one another in the mode by which the Cd micro fuel cells were recharged. A brief review of each mode and the results obtained therein are given below and in Table XV.

Details of the first operating mode were given earlier. Briefly, this involved a parallel charge circuit for the Cd micro fuel cells with protective diodes in each of the parallel branches to the Cd electrodes but without any protective diodes in the intercell connectors between Ag-Zn cells. Total operating time in this mode was 48 hours or 32 cycles. All components appeared to be functioning properly during the early stages of this first continuous cycle test. End-of-charge voltages of the Ag-Zn cells ranged from 1.96 to 2.15 volts and end-of-discharge voltages ranged from 1.45 to 1.66 volts. Appreciable outputs of as high as 100 mA (100 mA/cm^2) were noted from those Cd micro fuel cells in assemblies with end-of-charge voltages in excess of 2.05 volts. This signified consumption of oxygen at rates of as high as 21 cc/hr. The actual pressure rise in the silver-zinc cells was less than 0.703 Kg/cm^2 gage (10 psig). Some of the AgO micro fuel cells also exhibited appreciable output in the range of 30 to 40 mA for short periods (1-2 hours). This signified consumption of hydrogen at rates to 17 cc/hr. The presence of hydrogen in such amounts was unexpected in view of prior gassing studies.

TABLE XV

OPERATING CONDITIONS FOR CELLS ON 90-MINUTE CYCLE REGIME

Operating Time (hours)	Number of Cycles	Conditions for Operation
48	32	Initial operating mode, Figure 8.
50	33	Second operating mode with diodes between Ag-Zn cells (see Figure 9).
115	77	Third operating mode with transistors between Ag-Zn cells (see Figure 10).
696	455	Fourth and final operating mode with separate charge circuits for Cd micro fuel cells (see Figure 11).
909	606	Total operating time for three remaining cells since start.

After two days of operation, it became apparent that the Ag-Zn cells were rapidly approaching a state of unbalance. Those cells on the negative end of the stack tended to become overcharged while those on the positive end tended to become undercharged. It was realized that early cell failures would result from either excessive gassing of those cells on the negative end or reversal of those on the positive end. Therefore, it was decided to discontinue the test temporarily and investigate the cause for unbalance.

Two phenomena were subsequently uncovered which helped explain the origin of the unbalance. First, it was found that there were sizable leakage currents in each of the series connectors to the Ag-Zn cells. The leakage current was in the discharge direction of the silver-zinc cells and was noted to increase progressively from the negative to the positive end of the cell stack. The range in currents was from 30 mA between cells No. 7 and No. 8 on the negative end to 120 mA between cell No. 1 and No. 2 on the positive end. These leakage currents were stopped completely upon breaking the parallel charge circuit of the Cd micro fuel cells. Apparently, the parallel charge circuit of the Cd micro fuel cells was responsible for the intercell leakage currents. The indicated variation of these leakage currents also explained in part why the cells on the negative end tended to become overcharged and those on the positive end tended to become undercharged. A second observation which helped explain the unbalance was that of uneven distribution of current in the parallel Cd charge circuits. Those Cd micro fuel cells on the positive end of the Ag-Zn cell stack were noted to have much higher inputs than those on the negative end. Since the Cd electrodes were charged at the expense of the negative zinc electrodes of the Ag-Zn cell, these results also indicated that the zinc electrodes of the Ag-Zn cells on the positive end of the stack would be discharged more rapidly than those on the negative end. This also helps to explain why the unbalance developed in the indicated manner.

It should be pointed out that some variations in input to the Cd electrodes were to be expected, but not in the observed manner. Theoretically, it was surmised that those Cd electrodes which had been completely discharged would have less negative voltages and would thereby receive more current. This condition would prevail in the assemblies which had evolved large quantities of oxygen. In these early stages however, none of the Cd cells had been completely discharged. The variation in input must therefore have been caused by superimposition of Ag-Zn voltages upon the parallel Cd circuit.

The second mode of operation was carried out with the use of protective intercell diodes and a modified charge schedule for the Cd micro fuel cells. It was anticipated that these changes would prevent further unbalance of the Ag-Zn cells and provide more uniform current distribution to the Cd micro fuel cell electrodes. Total operating time in this mode was 50 hours or an additional 33 cycles. Leakage currents between Ag-Zn cells were stopped and current distribution to the Cd electrodes was much more uniform than above. It was noted however, that current distribution in the positive side of the Cd micro fuel cell charge circuit was very uneven (this is the current to the Zn negative electrodes). Here it was found that essentially all of this current was passing into the most positive zinc electrode and essentially no

current was entering other Zn electrodes. This was not considered serious at the time for it was rationalized that an even distribution was required only on the negative side of the parallel charge circuit.

Throughout the course of this phase of testing, the unbalance among the Ag-Zn cells continued to increase, but at a much lower rate than in the preceding phase. The most negative Ag-Zn cells became somewhat overcharged and the most positive cells became slightly undercharged. Because of the diodes, the overall voltage of the stack of 8 silver-zinc cells was much less than in the prior phase. In this case, the overall voltages ranged from 6.5 to 7.5 volts at 5 amps as compared with 12 to 14 volts at the same current in the first phase without diodes. Overall charge voltages however, were essentially the same in both cases in the range of 15 to 17 volts. The Cd micro fuel cells responded quite well in consuming oxygen in those cells which became overcharged and thereby limited the pressure rise. Until the very end of this phase, the maximum pressure developed in any one cell was only 1.27 Kg/cm^2 gage (18 psig) in Assembly No. 8. This was the most negative assembly which had become severely overcharged. During the final cycle, the internal pressure in this assembly exceeded 2.11 Kg/cm^2 gage (30 psig), which resulted in failure due to the case bursting. Cell voltage at this point was 2.12 volts. The excessive pressure rise occurred at this point even though the incorporated Cd micro fuel cell was operating quite effectively with an output of 50 mA and thereby consuming oxygen in excess of 10 cc/hr. This Ag-Zn cell had apparently become so overcharged that its O_2 gassing rate was more than could be accommodated by the existing micro fuel cells. The AgO micro fuel cells exhibited relatively low outputs throughout most of the phase. For the most part, the outputs ranged from 0 to 1 mA. This signified H_2 evolution and consumption rates from zero to 0.4 cc/hr. On a few occasions, however, there were noted to be short term increases in AgO output to 50 mA. This signified H_2 rates of up to 20 cc/hr. The pattern was quite erratic however, and no correlation could be made between H_2 rates and other parameters of the system.

Operation in the third mode was carried out for an additional 116 hours or 77 cycles. The new transistors were found to function quite effectively in this application. The voltage drop across each was only 0.1 volt at a discharge current of 5 amps. This was a significant improvement over the diodes which had given a voltage drop of 0.7 volts under the same conditions. For the seven assemblies, the overall discharge voltage was therefore almost 4 volts higher with the transistors than with the diodes. Aside from the improvements in discharge voltage there were no other major changes observed during this third phase of testing. The problem of unbalance of Ag-Zn cells still remained and became progressively severe during the course of cycling. Voltage of the cells on the positive end of the stack began to approach 1.0 volt at the end of the discharge and voltages of the cells on the negative end began to rise above 2.1 volts at the end of charge. It was interesting to note that the AgO micro fuel cells responded quite well in those cells with the exceptionally high end of charge voltages. Response of an AgO cell in such a case is given in Figure 21. Here it is noted that the Ag-Zn cell exhibited three distinct voltage plateaus on charge. The first was near 2.0 volts for the major portion of the charge. The second and third were near 2.1 and 2.4 volts at the end of charge. Output of the AgO micro fuel cell

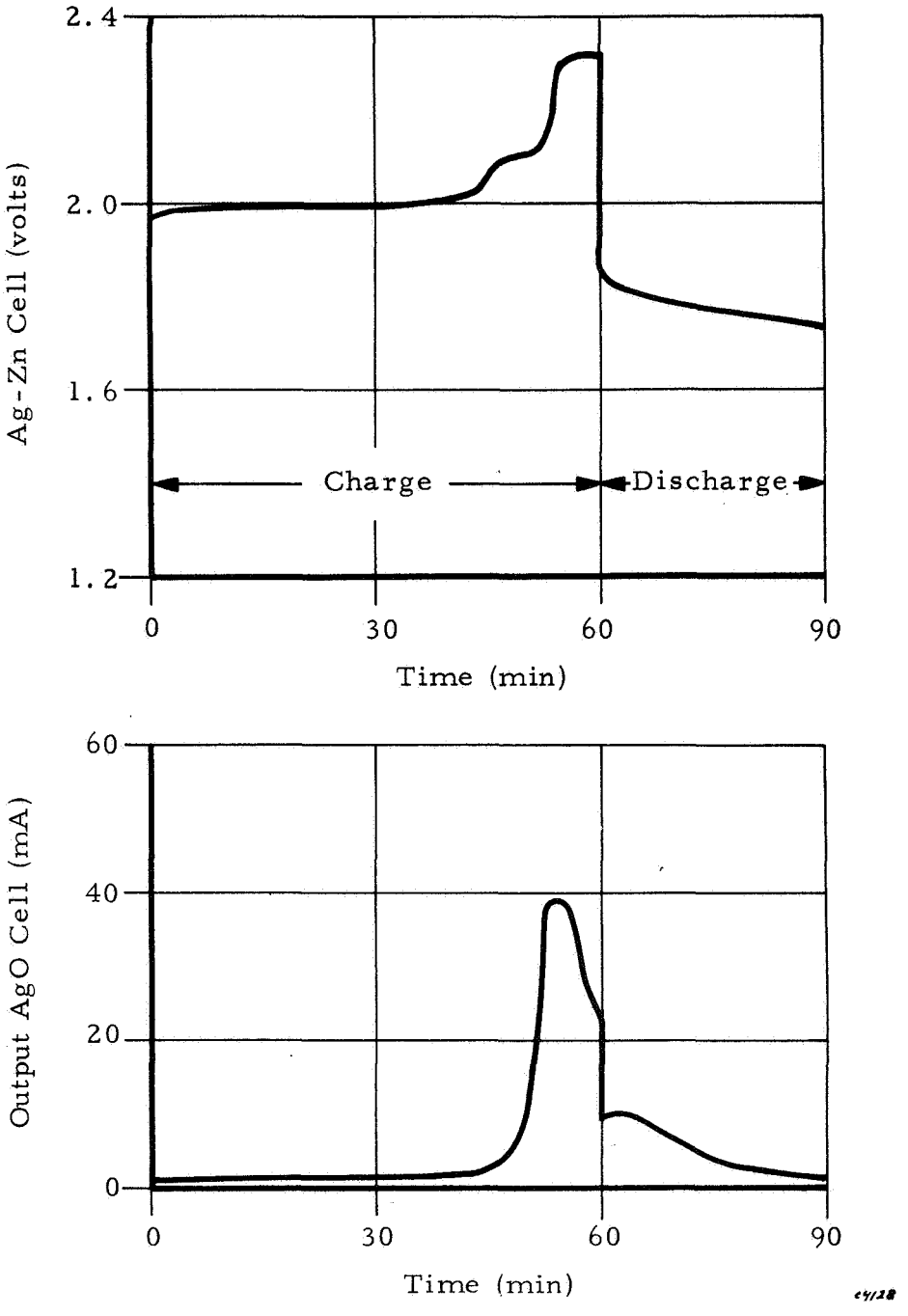


Figure 21. Response of AgO Micro Fuel Cell on Assembly Which Becomes Severely Overcharged (90-Minute Cycle Regime)

was noted to increase sharply as the charge voltage increased from the 2.1 to the 2.4 volt level. This upper plateau obviously represented the point where the negative zinc electrode of the Ag-Zn cell was fully charged and began to evolve hydrogen. The total amount of H_2 evolved during the cycle may be calculated by graphically integrating the current-time curve of Figure 21. The result is near 400 mA min which corresponds to approximately 3 cc H_2.

This third phase of testing was interrupted for several days during which an attempt was made to bring the cells back in balance. This was done by first discharging each completely to 1.0 volt and then carrying out repeat formation cycles on all cells. This was done in accordance with the formation procedures described earlier. Subsequent testing however, revealed that the problem of unbalance was still existent and continued to become more severe with increased number of cycles. Near the end of this phase, it was noted that Assembly No. 1, on the most positive end, had failed by reversal during an overnight run. Inspection of the automatic recorder tracings indicated that the voltage of this assembly became negative in the middle of a discharge period and internal pressure simultaneously increased to a level above 2.11 Kg/cm^2 gage (30 psig). This caused bursting of the cell case. The AgO micro fuel cell of this assembly had been noted to be functional prior to this reversal, but it apparently could not accommodate the excessive H_2 rates encountered here. A maximum of about 1.0 liter of H_2 could have been evolved during the course of such a cycle, which included a reversal, and the AgO micro fuel cell would have had to deliver over 3.0 amps to completely consume all of this H_2. This was beyond the capability of the currently employed AgO micro fuel cells.

The six remaining cells were subsequently carried through three additional formation cycles in preparation for the fourth and final test mode. This phase was carried out with a greatly simplified circuit. The parallel charge circuit for the Cd micro fuel cells was eliminated entirely and each was charged separately as required with an auxiliary power supply. Results obtained during this final period are given below.

During the early stages of the fourth and final phase, it was found that there was still an appreciable amount of unbalance amongst the remaining six cells. For this reason, it was decided to operate the cell stack initially at a lower voltage cutoff of 2.00 volts/cell. It was anticipated that continued cycling under these conditions might bring the cells back in balance without causing severe overcharge. In spite of this attempt, three cells did fail shortly thereafter and were removed from the cell stack. The causes of failure were internal short for one and excessive overcharges for the other. The fuel cells were operative in the latter assemblies, but could not accommodate the excessive gassing rates.

The three remaining cells did operate quite effectively after this point for an appreciable operating time (over 400 additional cycles). This was the longest continuous operating interval on this regime and yielded the most positive and significant results. An overall summary of this phase is given in Table XVI. Electrical balance of the AgO-Zn cells was quite well matched throughout most of the period. End-of-charge and discharge voltages of all

TABLE XVI

OVERALL SUMMARY OF REMAINING THREE ASSEMBLIES ON 90-MINUTE CYCLE REGIME

1.	Number of cells	3 cells
2.	Total number of cycles	606 cycles
3.	Total operating time	909 hours
4.	End of charge voltage range	1.92 - 2.20 volts
5.	End of discharge voltage range	1.42 - 1.62 volts
6.	End of charge current range	1.00 - 2.85 amps
7.	Discharge current range	4.25 - 5.40 amps
8.	Maximum press in a cell	1.27 Kg/cm^2 gage (18 psig)
9.	Output range of Cd cells	0 - 70 mA
10.	Output range of AgO cells	0 - 50 mA
11.	Maximum H_2 consumed in a cell	405 cc H_2
12.	Maximum H_2 pressure in a cell without AgO cell*	28.0 Kg/cm^2 (398 psi)
13.	Maximum O_2 consumed in a cell	1900 cc O_2
14.	Maximum O_2 pressure in a cell without Cd cell*	131.5 Kg/cm^2 (1370 psi)
15.	Maximum total pressure without AgO or Cd cells*	159.1 Kg/cm^2 gage (2269 psig)

*These are estimated pressures that would be developed in Assembly 3 without micro fuel cells after 765 hours assuming there is no chemical recombination of gases or reaction with silver-zinc electrodes.

three cells were within 0.03 volt of one another during this period. As a consequence, there were no cells which evolved exceptionally large quantities of gases. Rather, it was found that the gassing rates were more uniform and at the moderate levels found in the prior gassing studies of Phase I. All of the AgO micro fuel cells exhibited relatively low and continuous outputs near 1.0 mA. This was very close to the value that would have been predicted on the basis of the gassing studies and corresponded to H_2 rates near 0.4 cc/hr. Output of the Cd cells varied somewhat between cells and for a given cell during the course of a cycle. In general, however, the Cd outputs were found to vary in accordance with the end-of-charge voltages of their respective assemblies. Those assemblies with the desired end of charge voltages near 2.05 volts gave Cd outputs which averaged near 10 mA. A typical current trace of a Cd cell during this period is given in Figure 22. This shows a cyclical variation in output of the Cd cell with a maximum in the early portion of discharge and a minimum in the latter stages of charge. Maximum and minimum currents were 20 and 7 mA, respectively and average current was near 10 mA as indicated above. Corresponding average O_2 rate for this current level is near 2 cc/hr. This is also in accord with the prior gassing studies. Output currents of the three Cd cells and corresponding O_2 rates did vary somewhat from that shown in Figure 22 at different intervals during this final phase. These variations were most pronounced at the beginning and end of this phase when the cells exhibited unbalance. Those cells with high end-of-charge voltages above 2.05 volts exhibited higher Cd outputs to 70 mA while those with low end-of-charge voltages below 2.05 volts exhibited lower outputs in the range of 0 to 5 mA.

Charge currents to the Cd electrodes were varied during this final phase. Initial values were set at 20 mA per electrode, but this was found to be more than adequate. These values were subsequently reduced to a range between 10 and 15 mA which was found to be sufficient to accommodate the gassing rates. Total input to the Cd electrodes during this final phase (464 hours) ranged from a high of 6.8 Ah in one cell to a low of 4.9 Ah in another cell.

After nearly 700 hours (464 cycles) of continuous operation in this fourth phase, it was decided to stop the test and run capacity checks on the three remaining AgO-Zn cells. Cycling was stopped at the end of a charge cycle at which point each cell was discharged separately at 5.0 amperes to 1.0 volt. Results given below indicated that the cells had lost some of their original capacities which were near 22 Ah.

Cell Number	Capacity (Ah)
2	17.7
3	12.5
5	16.5

The cells were then carried through a formation charge at 0.7 ampere and then discharged again at 5.0 amperes with the following results.

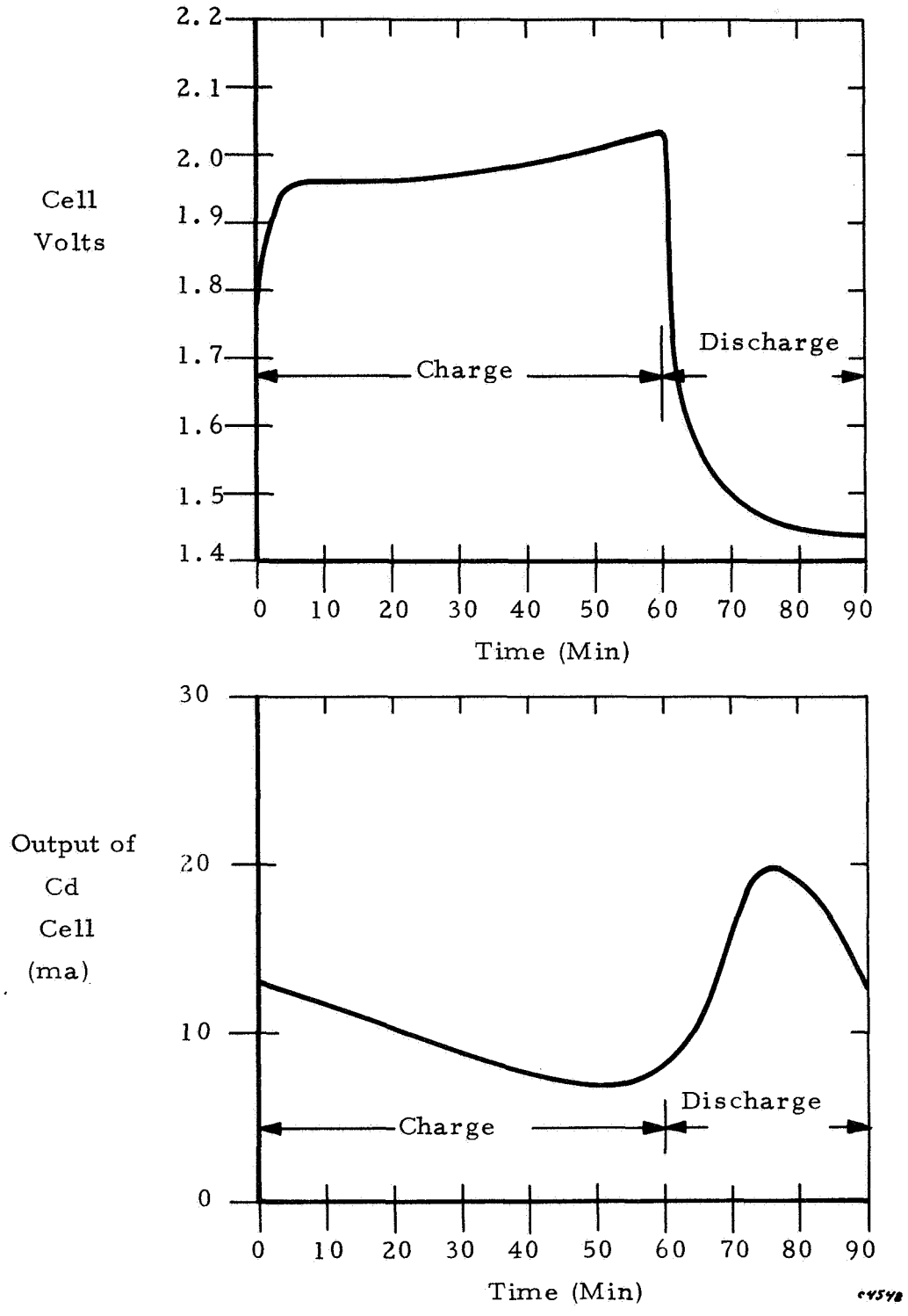


Figure 22. Characteristics of Cd Micro Fuel Cell on 90 Minute Cycle Test

Cell Number	Capacity (Ah)
2	15.0
3	2.9
5	0.0

These results indicated that Cells #3 and #5 had essentially failed after this formation charge while Cell #2 had shown an appreciable loss during this time. Cause of these failures was attributed to internal short circuit. This was not determined directly but was apparent from the voltage characteristics of the cells during these capacity tests.

The factors which led to these final failures could not be determined but it was strongly suspected that the major damage occurred during the earlier cycle tests which employed the parallel charge circuit for the Cd cells. High leakage currents and erratic AgO-Zn cell behavior were noted during these earlier periods, but not, however, during the final 700 hours when the parallel circuits were removed. It is further believed that the test would have yielded much longer cycle life characteristics had it been initiated in the final operating mode (with individual Cd charge circuits). An important recommendation for future work would be to establish this point experimentally.

A final point of discussion of this test regards overall effectiveness of the micro fuel cells in controlling pressure. This can be demonstrated best by calculating the maximum gas consumption in a given assembly and corresponding reduction in pressure by the micro fuel cells. The most extreme case was found to be that of Assembly #3. During the complete test (606 cycles or 909 hours), the Cd and AgO micro fuel cells on this assembly were found to have delivered outputs of 9.09 Ah and 966 mAh, respectively. These values correspond to consumption of 1900 cc O_2 by the Cd cell and 405 cc H_2 by the AgO cell. Without these micro fuel cells and assuming no chemical reactions, these amounts of gases would have resulted in pressure rise of 131.5 Kg/cm^2 (1870 psi) for O_2 and 28.0 Kg/cm^2 (398 psi) for H_2 for a final total pressure of 159.1 Kg/cm^2 gage (2269 psig). Although these values may be somewhat high due to neglect of chemical reactions, they do indeed illustrate the need for and effectiveness of micro fuel cells on this regime.

Stand Tests at 0°C

This test was carried out on four fully charged assemblies at 0°C in the manner described earlier. Open circuit voltages and micro fuel cell currents of each were monitored over a 143 day period or 3432 hours. The cells were then discharged for a final capacity check.

Results of the test are given in Table XVII. Open circuit voltages of two of the assemblies (#19 and #20) remained at 1.86 volts throughout the test. Open circuit voltage of the two other assemblies (#9 and #10) were noted to decline somewhat from the 1.86 volt level after the first 100 days. Final open circuit voltages were 1.80 volts for #9 and 1.85 volts for #10.

TABLE XVII

RESULTS OF STAND TESTS AT 0°C[1, 2, 3]

Time on Test (days)	Assembly #9		Assembly #10		Assembly #19		Assembly #20	
	Output AgO (μA)	Output Cd (μA)	Output AgO (μA)	Output Cd (μA)	Output AgO (μA)	Output Cd (μA)	Output AgO (μA)	Output Cd (μA)
0	50	5	50	2	50	4	100	1
1	1	1	2	1	1	0	1	2
3	10	0	5	0	5	0	5	0
6	10	0	10	0	5	0	0	0
8	10	0	10	0	4	0	0	0
10	5	0	3	0	2	0	0	0
13	20	2	10	2	10	2	2	0
15	20	2	10	0	10	0	5	0
17	20	0	10	0	10	0	5	5
20	20	0	10	0	10	0	5	0
22	20	1	10	1	10	0	5	0
27	20	0	10	0	10	0	5	0
30	20	1	10	0	10	0	10	1
36	10	1	10	1	5	0	5	1
41	20	1	10	0	20	0	5	1
52	20	1	5	1	5	1	3	1
70	20	1	3	1	5	1	3	1
90	20	1	5	1	3	0	3	1
111	10	2	5	2	2	0	2	1
125	15	2	5	2	2	0	5	2
136	15	3	3	2	1	0	2	2
143	10	2	3	2	2	0	2	5

(1) Initial open circuit voltages of all four AgO-Zn cells was 1.86 volts.

(2) Final open circuit voltages were 1.80 volts for #9, 1.85 volts for #10, 1.86 volts for #19, and 1.86 volts for #20.

(3) Internal pressures in all four assemblies were never greater than atmospheric.

Outputs of the fuel cells on all four assemblies were quite low throughout the test with the exception of the first day of stand. During this first day, the Cd cells exhibited appreciable outputs to 5 mA. This was attributed to consumption of the residual air in the assemblies. Thereafter, the output level of all the micro fuel cells declined to the micro ampere range. Inspection of Table XVII indicates that the AgO micro fuel cells exhibited outputs ranging from 0 to 20 μA. This signified H_2 rates of up to 0.2 cc/day. The cell with highest continuous output was noted to be on Assembly #9. Since it was also pointed out that this particular assembly exhibited the most pronounced decline in OCV, it is quite possible that there is a correlation between AgO current or equivalent H_2 evolution and OCV. Output currents of all the Cd micro fuel cells were noted to be much lower than the AgO cells and were within the range of 0 to 2 μA throughout. This signified maximum O_2 rates of only 0.01 cc/day.

During the prior gassing studies of Phase I at 0°C, it was noted that the same type of AgO-Zn cells evolved essentially no measurable quantities of gases via the water displacement technique. In these tests, however, we do have signs of extremely low, but nevertheless finite, quantities of gases being evolved. This difference could be explained on the basis that the micro fuel cells were sensing and consuming the evolved gases at a faster rate than they could recombine with the electrodes of the AgO-Zn cells. Evidently, only the latter was occurring in the water displacement tests.

The maximum amount of gas consumed in a given assembly was only 30 cc. This was in Assembly #9 and consisted of 29 cc H_2 and 1 cc O_2.

Final capacity tests were run after two additional weeks stand at room temperature. Results indicated that all four AgO-Zn cells had capacities near 8 Ah or 50% of rated capacity. These losses are not consistent with the results of the room temperature stand tests given below. No explanation can be offered for this at present.

Stand Tests at Room Temperature

This test was carried out on four fully charged assemblies at room temperature. Open circuit voltages and micro fuel cell currents of each of these assemblies were monitored over a 142 day period or 3408 hours. The cells were then discharged for a final capacity check.

Results of the test are given in Table XVIII. Open circuit voltages of all four assemblies were noted to remain at 1.86 volts throughout the test. Output currents of all the micro cells were quite low throughout, except during the initial phases when the outputs were higher because of residual gases in the assemblies. Currents from the AgO micro fuel cells were noted to vary somewhat among assemblies and from day to day on a given assembly. In general, however, these AgO currents were usually within the range of 10 to 30 μA. This signified H_2 rates ranging from 0.1 to 0.3 cc/day. Outputs of all the Cd micro fuel cells were generally much lower at levels of only 1 to 2 μA. This signified O_2 rates to only 0.01 cc/day.

TABLE XVIII

RESULTS OF STAND TESTS AT ROOM TEMPERATURE(1, 2 and 3)

Time on Test (days)	Assembly #21		Assembly #22		Assembly #23		Assembly #24	
	Output AgO (μA)	Output Cd (μA)	Output AgO (μA)	Output Cd (μA)	Output AgO (μA)	Output Cd (μA)	Output AgO (μA)	Output Cd (μA)
0	3000	0	6000	8000	6000	2000	8000	8000
1	30	0	60	240	50	30	60	60
2	10	0	20	20	20	10	20	20
5	0	0	40	30	20	10	30	20
7	10	60	30	10	20	5	10	10
9	5	0	5	0	2	5	10	3
12	0	0	20	10	10	5	10	2
14	0	0	10	2	10	2	20	2
16	0	0	20	2	10	2	10	2
19	0	0	10	1	10	2	10	2
21	0	0	10	1	10	1	10	1
26	1	1	20	1	10	1	10	10
30	0	1	10	1	10	1	10	5
35	1	1	10	1	10	1	10	2
40	0	0	20	1	10	1	10	2
50	0	0	20	1	10	1	10	1
70	0	0	10	1	10	1	10	2
91	0	0	10	1	10	1	10	2
106	30	0	20	1	10	1	10	2
120	30	1	20	1	10	1	15	2
132	20	1	15	0	10	1	10	1
142	20	0	15	0	10	1	15	1

NOTE: 1. Initial open circuit voltages of all four AgO-Zn cells was 1.86 volts.

2. Final open circuit voltages of all four AgO-Zn cells was 1.86 volts.

3. Internal pressures in all four assemblies was never greater than atmospheric.

Again, it will be noted that these results are not exactly consistent with the results of the gassing studies on the same type of cell in Phase I. There it was shown that after a brief period the gassing rates of all the cells were essentially zero. In this test, however, we again have signs of small but finite quantities of gases being evolved. In order to account for this, we can only say once again that the micro fuel cells must have consumed the gases at a faster rate than they could react with the electrodes of the AgO-Zn cells.

Final capacity tests revealed that all four AgO-Zn cells had maintained near 19 Ah or 85% of their original formation capacity for the complete stand period.

FEASIBILITY OF MICRO FUEL CELL TECHNIQUE

Results to this point have demonstrated only that the micro fuel cells are effective in controlling pressure in sealed storage cells. This is a necessary but not sufficient proof of the overall feasibility of employing micro fuel cells in a practical spacecraft power system including the solar array and storage cells. In order to demonstrate this point, it will be necessary to examine the possible interactions that the micro fuel cells will have on the complete system. These include the effects of micro fuel cell weight, power and maintenance requirements on the design and performance requirements of the overall power system. It is also necessary to show that the micro fuel cells do not cause any degradation of the storage cells and thereby cause more reliability problems. Finally, it is worthwhile to compare micro fuel cells with other devices and techniques for controlling pressure in the storage cells.

Let us first examine the weight penalties associated with use of micro fuel cells. Total weight of the complete dual micro fuel cell assembly developed on this program was noted to be 35 grams. This includes weight of the two micro fuel cells and their adapter. Total weight of the unsealed 16 Ah AgO-Zn cell was 285 grams. We can therefore calculate that there is a 12% weight penalty associated with use of the existing micro fuel cell assemblies. This penalty could be reduced even further if it were possible to incorporate the micro fuel cells directly inside the AgO-Zn cells rather than inside the adapter. This could be done with minor modifications of the case and terminals of the AgO-Zn cell. Estimated total fuel cell weight in this case is only 20 grams, or 7.0% of total AgO-Zn cell weight.

It is also worthwhile to examine the effects that the above weight penalties have on energy densities of the AgO-Zn cells. Table XIX indicates that energy density of the unsealed 16 Ah cell is 84.6 watt-hrs/Kg (38.5 watt-hours/lb.). This was taken as the ratio of nominal output (16 Ah at 1.5 Volts) to overall weight of 285 grams. A relatively small degradation in energy density is noted for sealing the cell with improved micro fuel cells to 78.6 watt-hours/Kg (35.8 watt-hours/lb.). There is also noted to be a relatively small degradation to 75.1 watt-hours/Kg (34.2 watt-hours/lb.) for sealing the cell with the existing micro fuel cell assembly. These results establish that the use of micro fuel cells does not cause an appreciable loss of energy density in AgO-Zn cells. This is a significant point from the view of power system design, for it permits essentially fulluse to be made of the intrinsic high energy density of the AgO-Zn system.

Another important consideration is that of power requirements for charging the micro fuel cells. One may readily question whether these requirements will place an excessive burden on the solar array and/or will require the use of auxiliary electronic equipment which will detract from the usefulness of the micro fuel cells.

Before we attempt to answer these questions, it will be necessary to specify the particular cycle regime of interest. For the sake of this discussion,

TABLE XIX

ENERGY DENSITIES OF SEALED AgO-Zn CELL

Method of Sealing	Energy Density* (watt-hrs/Kg)	Energy Density* (watt-hrs/lb.)
1. No sealing	84.6	38.5
2. Improved Dual Micro Fuel Cell Assembly	78.6	35.8
3. Existing Dual Micro Fuel Cell Assembly	75.1	34.2
4. Potting with Epoxy as per Manufacturers Specifications	43.5	19.8

* NOTE: These are calculated energy densities for a high rate 16 Ah AgO-Zn cell with nominal capacity of 24 W-h and weight of 285 grams.

we will divide all regimes into two classes consisting of the mild and rigorous types. The mild type will refer to long cycles at low depths of discharge such as the 24-hour regime described previously. This will also include regimes with long float charge periods, such as in IMP satellite applications (Reference 3). The rigorous type will refer to rapid cycles at moderate to high depths of discharge such as the 90-minute regime given previously.

In the case of mild regimes, we have found extremely low H_2 rates and moderate to low O_2 rates. Under these conditions, it was possible to operate both AgO and Cd cells in the primary mode (without recharge) for quite extended periods. Depending on the details of the regime and operating time, it is entirely possible that both micro fuel cells may be operated in the primary mode throughout the entire space mission. Under these conditions, there are no power requirements for the micro fuel cells and they may be operated entirely independently of the main power supply. For extended missions on mild regimes, it may, however, be necessary to supply a low rate trickle charge to the Cd micro fuel cells. As will subsequently be shown, this charge can be supplied by the AgO-Zn cell itself (we have termed this the parasitic charge). This again avoids the need for use of the main power supply and any auxiliary equipment. It is also possible to apply a trickle charge to the AgO micro fuel cell in the same manner if required on an extended mission.

In the case of rigorous regimes, we have found increased but yet relatively low H_2 rates and greatly increased O_2 rates. Under these conditions, it was possible to operate the AgO cells for extended periods in the primary mode. For very long missions, it may be necessary and is also possible to supply a parasitic trickle charge to the AgO cells as above. There are therefore essentially no power requirements for the AgO micro fuel cells on a rigorous regime.

Charge currents for the Cd cells on this type of regime are appreciably higher than any of the above because of the exceptionally high O_2 rates. These requirements may be in the range of 0 to 50 mA per cell or greater, depending upon the actual conditions. The most practical method of supplying these charge currents is via the parasitic method. As will subsequently be explained, however, this process was not fully developed at the time it could have been employed in these tests. The most practical alternative at the time appeared to be that of charging all of the Cd cells in parallel with one auxiliary supply. This method, however, was found to result in leakage currents and degradation of the AgO-Zn cells. It was not clearly demonstrated that this charge process was fundamentally unsound, but that the problems involved in making it work properly appeared formidable. It is still possible that an effective parallel charge circuit could be designed for this purpose. This would provide a reasonable method for charging the Cd micro fuel cells which does not detract from their usefulness. Overall size and weight requirements for such an auxiliary supply would be quite small as it would have to supply less than 0.1 watt per Cd micro fuel cell. During the course of this program, it was necessary to resort to the use of separate power supplies to charge each of the Cd micro fuel cells. Although this technique did accomplish the objective, it is by no means ideal from a power systems point of view. Required sizes of these supplies would not be the limitation here, but their number and complexity could cause serious reliability problems.

At this point, it does appear that the parasitic charge technique is the most ideal micro fuel cell charging process from the viewpoint of a practical power system. It has been found that currents up to 50 mA can be supplied in this manner to both Cd and AgO micro fuel cells. This would have been more than adequate to accommodate the O_2 gassing rates on the 90-minute and other similar rigorous regimes. The parasitic charge processes are carried out by simply making external contacts between appropriate electrodes of AgO-Zn cells and micro fuel cells. Suitably designed wicks provide for the high currents indicated above. Charge occurs spontaneously and is self-regulating in preventing overcharge.

In summarizing this part of the discussion, we believe that either the parasitic charge method or the parallel charge method with one small power supply would be feasible for a practical space power system. Neither one of these would interfere to any major degree with the overall power system and would not detract from the advantages of micro fuel cells. Of the two, we believe the parasitic charge method to be the simplest and most reliable at this time.

There are absolutely no maintenance requirements for operating the micro fuel cells in the primary mode. The units were merely installed in the batteries and placed on load. This automatically activates them for consumption of gases. Neither are there any maintenance requirements for operation of the micro fuel cells in the secondary mode via parasitic recharge. When properly connected, the charge and discharge processes occur automatically and simultaneously. Some maintenance was required in carrying out the charge processes on this program. This involved manual switching to start and stop the charge as required. Although it would be possible to develop an automatic switching process for this purpose, this is not justified on the basis of the questionable feasibility of the process as described above.

A final point concerns the possible degradation of the AgO-Zn cell by the micro fuel cells. The only occasion during which this phenomenon was observed was during the operation with the parallel charge circuit as described above. Rapid loss of capacity of the AgO-Zn cells was noted during these periods. Cause of this degradation was, however, noted to be with the electrical circuit and not the fuel cells per se. No other signs of degradation were ever observed for operating the micro fuel cells in the primary mode or in the secondary mode with a separate power supply for each cell. Verification of these points is evident from the results of the 24-hour cycle test which employed both of these methods. The AgO-Zn cells on this test completed 3792 hours or 158 cycles and were still in good working order at the end. Final capacity tests indicated that three of these had maintained at least 19 Ah of their original capacity.

In summarizing this part of the discussion, we have shown that with proper methods of installation and operation the micro fuel cells will cause little if any interference with the design of the overall power system and will cause little if any degradation in performance of the system. Conversely, the micro fuel cells contribute significant improvements to the overall system.

In addition, to establishing feasibility of the micro fuel cells, it is also worthwhile to compare them with other devices and techniques for controlling pressure in sealed AgO-Zn cells. These comparisons are not quite so simple, however, because all of the new methods, including micro fuel cells, are in the early stages of development. No performance tests are available yet on actual flight cells which employ these devices and techniques. The comparisons which are given below are therefore only semiquantitative at best.

One approach has been to develop AgO-Zn cells which evolve less gases and also exhibit higher combination rates of H_2 and O_2 with the electrodes (References 4, 5). These improvements are brought about by use of such additives to the electrodes as HgO and PdO and minimizing the amount of free electrolyte which is the most important factor regarding recombination. The latter is accomplished with the use of more porous electrodes and auxiliary separators which contain more electrolyte. When such cells are potted with a suitable sealant, such as epoxy, they can be successfully operated over a range of regimes in the sealed condition.

Although this approach yields satisfactory operation in the sealed condition, it does so at the expense of an appreciable reduction in energy density. Inspection of Table 19 indicates that the method causes a degradation of almost 50% of usable energy density from 84.6 to 43.5 watt-hours/Kg (38.5 to 19.8 watt-hours/lb.). This penalty reduces the attractiveness of AgO-Zn cells for many potential missions. If this value of energy density were employed in the analyses of Bacher (Reference 6) it would be found that the AgO-Zn cell has no particular advantages over the AgO-Cd cell for most orbiting regimes and may not even be as good as the Ni-Cd for some regimes because of the lower cycle life of the AgO-Zn system. Micro fuel cells on the other hand cause very little degradation in energy density and thereby permit full advantage to the taken of the intrinsic high energy of the AgO-Zn system.

A second approach involves use of auxiliary electrodes to aid in consumption of evolved gases and also to be used as charge control devices to prevent overcharge and resultant gassing. The most effective auxiliaries have been found to be the platinum fuel cell electrodes. These apparently function well for some time, but are eventually found to cause degradation of the Zn electrodes and subsequent evolution of hydrogen. The approach has apparently been abandoned by most investigators until improved non-platinum type auxiliaries can be developed. In the event that such auxiliaries are perfected, they could be competitive with micro fuel cells in this application. Both types of devices would contribute very little weight penalties and neither would add appreciably to the power requirements or complexity of the power system. Some auxiliaries would be required for the charge control function of either auxiliary electrodes or micro fuel cells. The requirements should be the same in both cases, however, as both operate on the same principles. The charge control function of micro fuel cells is being developed on an internal program.

A third approach involves use of charge control techniques which are based on current-voltage characteristics of the AgO-Zn cells rather than their gassing characteristics on overcharge. The process is quite effective

when applied to the low gassing rate type of cells described above. Hennigan, who has developed the process (Reference 3), has described it as a two-step process wherein applied charge voltage is reduced from a higher to a lower level when charge current has tapered to a pre-determined cutoff point. The process prevents unbalance and subsequent gassing that would occur if the cells were left on continuous float charges. These conditions would otherwise prevail on IMP satellites which are subjected to long periods of sunlight. Hennigan has shown the process to be quite effective in controlling gassing in AgO-Cd cells and is applying it to AgO-Zn cells (Reference 3).

We cannot compare the micro fuel cell with this technique at this point because we lack sufficient data on AgO-Zn systems. We can, however, point out that perhaps a combination of the micro fuel cell and this charge control technique would prove to be the most reliable and feasible system. The charge control system would prevent unbalance and overcharge which account for the major portion of the gassing. The micro fuel cells would then accommodate any gases that result from nonelectrochemical sources (degradation of electrodes) and would also serve as insurance to accommodate short term electrochemical gassing which could result from "maverick" cells.

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